RICE UNIVERSITY

The Coupling of the Carbon and Nitrogen Cycles in Agriculture: Crop Ecosystem Oxidative Ratio and the Effects of Fertilization on Biofuel Feedstock Quality

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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HOUSTON, TEXAS
NOVEMBER 2010

ABSTRACT

The Coupling of the Carbon and Nitrogen Cycles in Agriculture: Crop Ecosystem Oxidative Ratio and the Effects of Fertilization on Biofuel Feedstock Quality

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Agriculture significantly impacts the global carbon (C) and nitrogen (N) cycles through land use change, soil C loss, greenhouse gas emissions, and increased fixed-N availability. Agriculture occupies a third of the terrestrial biosphere, making understanding its impacts on the C and N cycles critical. I used a novel analytical tool (solid-state ^{13}C nuclear magnetic resonance spectroscopy) to characterize properties of the C and N cycles in agriculture, including biochemical responses to N fertilizer and agriculture gas fluxes.

A central component of the C cycle is the rapid exchange of carbon dioxide (CO_2) and oxygen (O_2) between the terrestrial biosphere and the atmosphere. Gas flux O_2/CO_2 ratios (oxidative ratio–OR) vary depending on ecosystem type, plant species, and nutrient status. It is necessary to constrain OR to assess the uptake of anthropogenic CO_2 by the terrestrial biosphere and ocean. I measured the OR of the top three crops in the United States (soybean, corn, and wheat) and found significant variability. I additionally tested the effect of N fertilizer application on corn ecosystem OR and on the difference between respiration and photosynthesis OR and observed no detectable changes. Conversely, soil organic matter OR is different from gas flux OR values, likely due to the influence of past land use and fractionation of OR during decomposition.

I also analyzed how anthropogenic inputs to the N cycle (N fertilizer) and sustainable agriculture practices (cover crop) change plant biochemistry. This work has immediate implications for the biofuel industry. A central challenge to cropping for cellulosic ethanol feedstocks is the potential environmental damage from increased fertilizer use. I showed that yield increases in response to fertilization are not uniform across biochemical classes (carbohydrate, protein, lipid, lignin) or tissues (leaf and stem, grain, reproductive support). Heavy fertilizer application yields minimal grain benefits and almost no benefits in residue carbohydrates, while degrading the cellulosic ethanol feedstock quality and soil C sequestration capacity. Further cost analysis of these results showed that it is not cost-effective for farmers to apply high levels of N fertilizer, whether the crop is intended for food or fuel.

ACKNOWLEDGEMENTS

I am extremely grateful to my advisor, Dr. Caroline Masiello, for her knowledge, guidance, understanding, and support during my tenure at Rice University. I could not have asked for a kinder, more considerate and supportive advisor. I have learned so much under her guidance, not just in the biogeochemistry field, but also on how to be an exceptional leader and the keys to a successful academic career. She has been and will continue to be an amazing role model for me.

I am also thankful for the chance to collaborate with Dr. Bill Hockaday while he was a postdoctoral researcher in our group. He was amazingly helpful, teaching me how to operate the Bruker nuclear magnetic resonance (NMR) spectrometer and understand my results. His vast knowledge never ceases to amaze me, nor his willingness to stop what he was doing to answer a question and patience when I kept bugging him in his office.

Furthermore, I would like to thank my committee members, Dr. John Anderson (Earth Science), Dr Cin-Ty Lee (Earth Science), and Dr. Jennifer Rudgers (Ecology & Evolutionary Biology) for their support and feedback. I would also like to thank my coauthors Dr. Jeff Baldock (CSIRO), Dr. Sieg Snapp (MSU/KBS-LTER), and Dr. Claire McSwiney (KBS-LTER) for sharing their knowledge in NMR and agronomy with me.

I am grateful to my group members who have assisted me during my time here through help with sampling, grinding tons of biomass, data collection, proofreading papers, and being good listeners. They include: Fanwei Zeng (the perfect officemate), Bill Hockaday, Krystle Hodge, LaQuanti Calligan, Nita Clark, Lacey Pyle, Sarita Minor, Becca Barnes, Willy Xu, and Paul Tucker.

Funding for my research was provided by the National Science Foundation (DEB-0445282; DEB-0614524). Additional support was provided by the NSF Long-Term Ecological Research (LTER) Program at the Kellogg Biological Station (KBS) and by the Michigan Agricultural Experiment Station. I thank Dr. Phil Robertson and the KBS-LTER staff, specifically Drew Corbin and Stacey VanderWulp, for assistance with sampling. I am grateful to Dr. Larry Alemany for help with training and using the Shared Equipment Authority's Bruker NMR spectrometer. I would also like to thank Dr. Wayne Polley at the USDA-ARS in Temple, TX for collaborating with Bill and I and allowing me to sample the CO_2 Tunnel Experiment.

My sanity would probably be in question at this point without the support of my friends and family. I would like to thank Sagar Bhatt, Rachel Bilyeu, Shawn Bilyeu, and Brittany Mitchell for always being there for me and helping me cut loose. I am also extremely grateful to my boyfriend, Ryan Schweller, and for his ability to tolerate my rants, and always make me smile. He made sure I ate, got some sleep, and relaxed and had fun every once in a while, and for that I thank him.

I would like to thank my family for all their support and encouragement, including my grandparents, Al & Nancy Bevacqua and Frank & Margaret Gallagher, my sister-in-law, Britani Gallagher, and all my aunts, uncles, and cousins. I would also like to thank my brothers, Ian and Devan Gallagher, for always encouraging me. Whenever they are around, life is better.

Last, but most importantly, I would like to thank my parents, Michael and Melissa Gallagher. Without them I would not be here. They have taught me so much. Everything they have done for me has allowed me to succeed. I will always be eternally grateful to them.

I dedicate my thesis to my parents,

Michael and Melissa Gallagher.

TABLE OF CONTENTS

LIST OF TABLES

Appendices

LIST OF FIGURES

Chapter 3

Chapter 4

Appendices

LIST OF ABBREVIATIONS

C – carbon

N – nitrogen

H – hydrogen

O – oxygen

CHNO – carbon, hydrogen, nitrogen, oxygen

CO_2 – carbon dioxide

O_2 – atmospheric oxygen

CH_4 – methane

N_2 – atmospheric nitrogen

N_2O – nitrous oxide

NO_x – nitrogen oxide

Nr – reactive nitrogen

NO_3^- – nitrate

NH_4^+ – ammonium

NH_3 – ammonia

NH_4NO_3 – ammonium nitrate

SO_4^{3-} – sulfate

PO_4^{3-} – phosphate

OR – oxidative ratio

OR_{net} – net oxidative ratio of the terrestrial biosphere

OR_{ab} – photosynthesis oxidative ratio

OR_{ba} – decomposition/respiration oxidative ratio

F – carbon gas flux

NPP – net primary production

C_{ox} – carbon oxidation state

EA – elemental analysis

CHNS/O – carbon, hydrogen, nitrogen, sulfur/oxygen

^{13}C NMR – solid-state ^{13}C nuclear magnetic resonance spectroscopy

MAS – magic angle spinning

CP – cross polarization

DP – direct polarization

CP-MAS – cross polarization-magic angle spinning

DP-MAS – direct polarization-magic angle spinning

SSB – spinning side band

C_{obs} – observable carbon

HF – hydrofluoric acid

MMM – Molecular Mixing Model

USDA – United States Department of Agriculture

U.S. – United States

IPCC – Intergovernmental Panel on Climate Change

KBS-LTER – Kellogg Biological Station – Long Term Ecological Research

MAT – mean annual temperature

M – mass

R1 – replicate 1 (Rep 1)

R2 – replicate 2 (Rep 2)

R3 – replicate 3 (Rep 3)

R4 – replicate 4 (Rep 4)

%RSD – percent relative standard deviation

ANOVA – analysis of variance

ANCOVA – analysis of covariance

FUE – fertilizer use efficiency

GPS – global positioning system

NIRS – near infrared spectroscopy

LIST OF DEFINITIONS

Biochemical: chemical compounds biologically produced, examples include carbohydrate, protein, lignin, and lipid

Biochemical Stock: total mass of a biochemical produced by an organism

Carbohydrate: compound with general formula $C_n(H_2O)_n$; includes compounds such as glucose, sucrose, fructose, cellulose; cellulose is the most abundant biochemical

Protein: polymers of amino acids (i.e. the amino (NH_2) and carboxylic acid (COOH) groups are attached to the same C atom); protein biomolecules account for most of the N in plants

Lignin: rigid biochemical primarily found in cell walls; used by higher plants to provide support; derived from monosaccharides; second most abundant biochemical

Lipid: broadly, biomolecules that are insoluble in water but extractable by solvents; can include fats, waxes, triglycerides, steroids, aliphatic carboxylic acids and alcohols

Carbon Oxidation State (C_{ox}): a numerical value that describes the bonding environment of C in biomolecules; values range from $^{-}4$ – $^{+}4$

Oxidative Ratio (OR): ratio of moles of atmospheric oxygen to moles of carbon dioxide; values range from 0 – 2

For photosynthesis: $$\frac{\text{moles of } O_2 \text{ released}}{\text{moles of } CO_2 \text{ consumed}}$$

For respiration, decomposition, etc.: $$\frac{\text{moles of } O_2 \text{ consumed}}{\text{moles of } CO_2 \text{ released}}$$

(Killops and Killops 2005)

CHAPTER 1

Introduction

This thesis investigates the coupled interactions between the carbon (C) and nitrogen (N) cycles within the context of agriculture. Agricultural ecosystems comprise over a third of the terrestrial biosphere, and their management manipulates both the C and N cycles to increase crop productivity; this manipulation is critical to sustaining food supply and the biofuel industry. Interactions between these cycles and agriculture impact climate, energy and food security. To address issues related to climate change, energy and food security, C and N cycle impacts cannot be addressed separately, but need to be considered in a coupled biogeochemical approach.

My thesis investigates the interactions between the C cycle, N cycle and agriculture in three ways. First, I analyzed how crop species, and agricultural management strategy (N fertilization, or use of cover crop) influence the gas exchange fluxes, or the oxidative ratio (OR), of the ecosystem. Only approximately half of anthropogenic CO_2 remains in the atmosphere, with the rest going to the terrestrial biosphere and ocean C sinks. Constraining the terrestrial biosphere OR value is critical to understanding the global fate of anthropogenic carbon dioxide (CO_2). Understanding where anthropogenic CO_2 is going within the C cycle and the mechanisms that control this is critical to our developing C management strategies. My estimations of agricultural ecosystems' OR is a critical first step in this process. Second, I analyzed how anthropogenic additions of N in agriculture (i.e. N fertilization) impact corn plant biochemistry (carbohydrate, protein, lignin, and lipid), and quantify the yield implications for the biofuel industry. Finally, I expanded on these biofuel implications through a cost assessment model I used to determine how agricultural management techniques (level of N fertilization, or use of a cover crop) influence the cost-efficiency of growing corn depending on what the crop is intended for (grain ethanol, food, or cellulosic ethanol). I performed this research at the Nitrogen Rate Experiment at the National Science Foundation-funded Kellogg Biological Station-Long Term Ecological Research Site (KBS-LTER) in Michigan, USA. This study was designed to measure how different N fertilization rates (kg N ha^{-1}) affect both crop yields and the environment, and how these effects change if a cover crop (winter wheat) is added. I used C and N organic geochemical tools (e.g. ^{13}C nuclear magnetic resonance, CHNS/O elemental analysis) to understand the mechanisms by which agricultural ecosystems and management techniques affect the C and N cycles through altering plant biochemistry and gas exchange fluxes (OR).

For the rest of this chapter, I will provide background on the C and N cycles. I will also discuss agricultural ecosystems, and their environmental impacts and roles in the biofuels industry and the C and N cycles.

The Carbon Cycle

The C cycle can be abstracted as three major dynamic C pools (the atmosphere, terrestrial biosphere, and ocean), the fluxes between these pools, and C pools that remove C from this cycling (geologic C and ocean C burial; Fig. 1). Since ~1880, atmospheric CO_2 concentrations have been increasing from ~280 ppm in the early 19th century to 379 ppm in 2005 (Alley et al. 2007) due to anthropogenic CO_2 emissions primarily from fossil fuel combustion (Fig. 2).

How increasing atmospheric CO_2 will affect the terrestrial and ocean biospheres remains unclear. Increasing atmospheric CO_2 is currently decreasing ocean pH, (Ruttimann 2006; Orr et al. 2005), altering terrestrial ecosystem composition (Polley et al. 2003; Polley et al. 2002), plant growth patterns (e.g. Hamilton et al. 2002; Norby et al. 2004), and the food web (Emmerson et al. 2005). CO_2-driven climate change is also predicted to change our environment by reducing polar ice caps and sea ice extent, increasing sea level, changing shorelines, and shifting ecosystem-latitudinal extent (Prentice et al. 2001; EPA 2006a). These environmental impacts will have significant impacts on society through disease vector movement, population relocation near shorelines, increased mortality rates during extreme heat events, and increased famines (EPA 2006b). Understanding the C cycle and the fate of anthropogenic CO_2 in the environment is critical to accurately predicting these impacts.

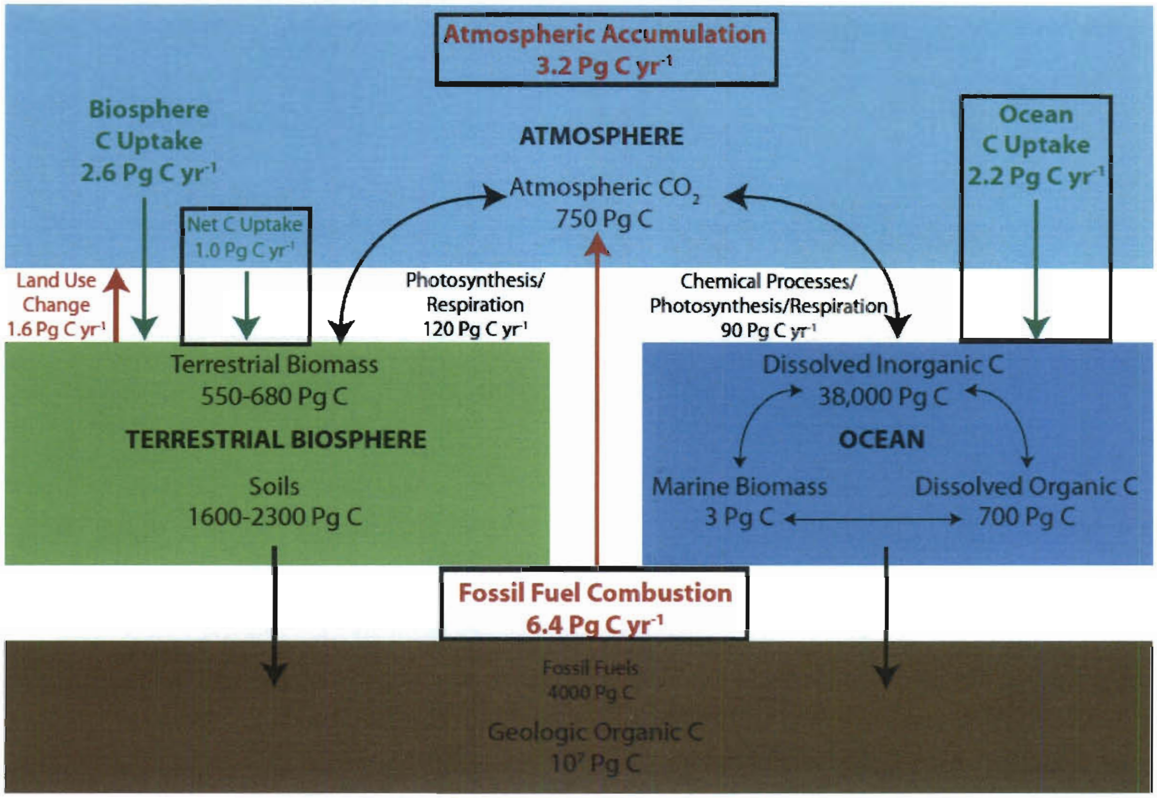

Figure 1. The Carbon Cycle during the 1990s

Adapted from the Intergovernmental Panel on Climate Change's Third and Fourth Assessment Reports. For 2000-2005, Atmospheric Accumulation rates of CO_2 have increased from 3.2 ± 0.1 Pg C yr^{-1} to 4.1 ± 0.1 Pg C yr^{-1}, corresponding to release rates to the atmosphere from fossil fuel combustion rate of 6.4 ± 0.4 Pg C yr^{-1} and 7.2 ± 0.3 Pg C yr^{-1}, respectively. Apportionment calculations split the difference between the fossil fuel combustion release rate and the atmospheric accumulation rate for the 1990s between the terrestrial biosphere (net uptake 1.0 ± 0.6 Pg C yr^{-1}) and the ocean (net uptake 2.2 ± 0.4 Pg C yr^{-1}. The net uptake rate of the terrestrial biosphere takes into consideration release of C to the atmosphere due to land use change (1.6 Pg C yr^{-1}). See (Denman et al. 2007; Prentice et al. 2001).

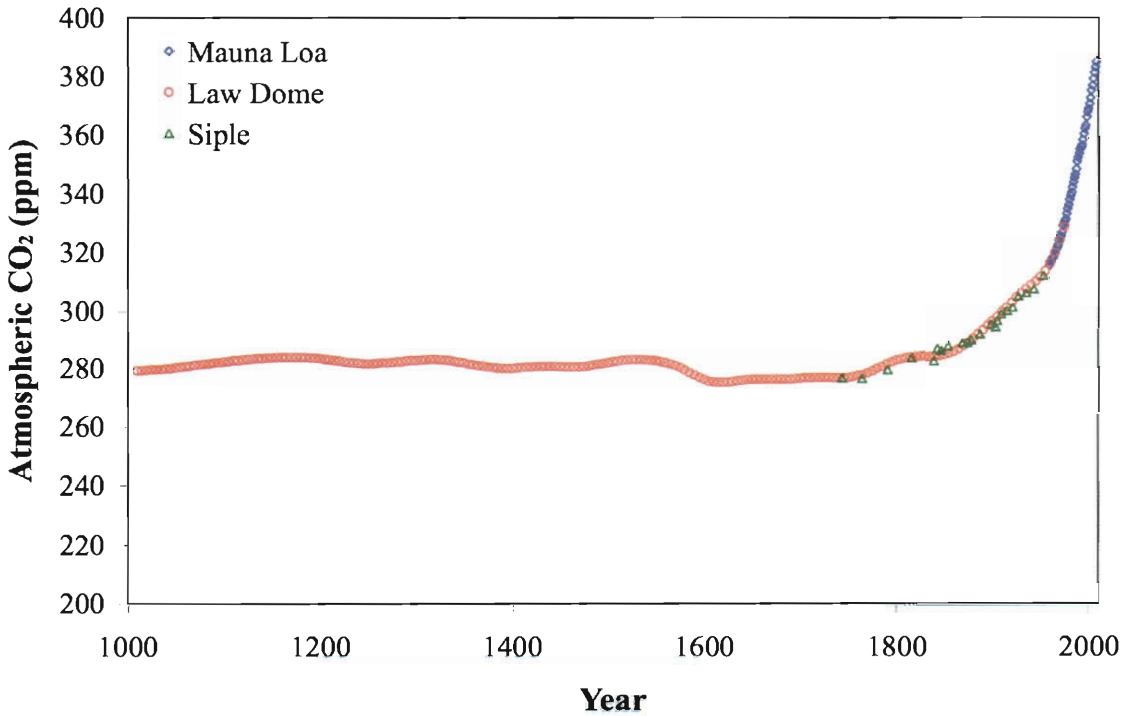

Figure 2. Atmospheric Carbon Dioxide Concentrations with Time

The industrial revolution began a significant anthropogenic source of CO_2 to the atmosphere from fossil fuel combustion. Data were downloaded from the Carbon Dioxide Information Analysis Center – http://cdiac.ornl.gov. The figure is adapted from CO_2 measurements from ice cores taken at Law Dome, Antarctica (Etheridge et al. 1998) and Siple Station, Antarctica (Neftel et al. 1994) and atmospheric measurements made at Mauna Loa, Hawaii (Keeling et al. 2009).

Anthropogenic CO_2 Apportionment

Anthropogenic CO_2 emissions to the atmosphere are being partially compensated for by two C sinks: the terrestrial biosphere and the ocean (Tans et al. 1990; Keeling et al. 1996; Manning and Keeling 2006). The sizes of these sinks can be calculated using atmospheric O_2 and CO_2 records (Fig. 3; Keeling and Shertz 1992; Keeling et al. 1996; Bender et al. 1998; Battle et al. 2000; Manning 2001; Bender et al. 2005; Manning and Keeling 2006).

It is critical to understand the time-varying fate of anthropogenic CO_2 in the C cycle for several reasons. One, it helps determine if the terrestrial biosphere and oceans are increasing, maintaining, or decreasing their C uptake rates (Le Quere et al. 2009; Raupach et al. 2008). Two, improved understanding of the terrestrial and ocean C uptake rates and their mechanisms will help develop effective C management strategies (e.g. improving land management (Smith 2004), greening the oceans (Bakker 2004) or protecting vulnerable C reservoirs (Schuur et al. 2009). Finally, understanding the separation of anthropogenic CO_2 between reservoirs allows for improved climate forecasts (Manning and Keeling 2006).

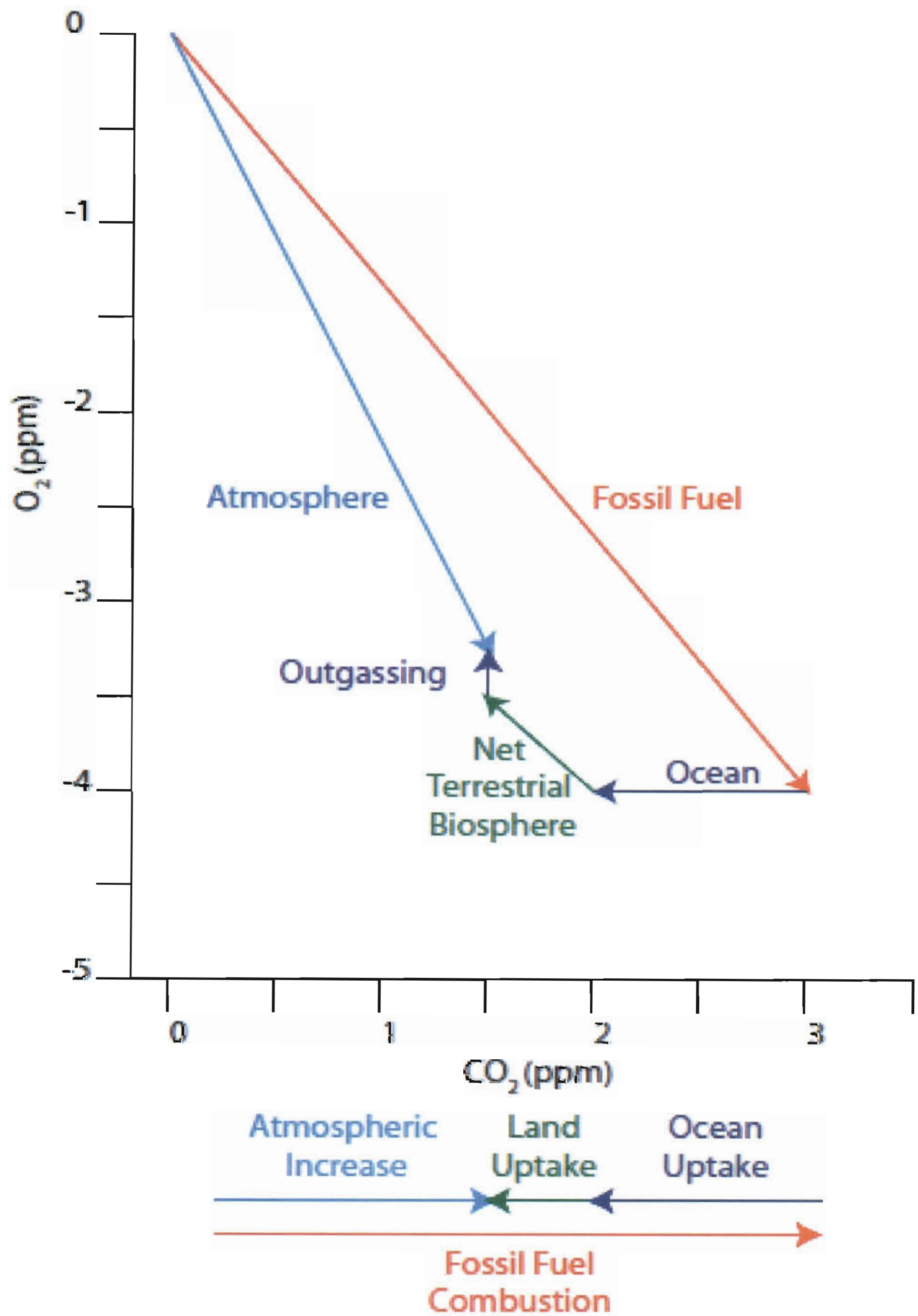

Figure 3. Anthropogenic CO_2 Apportionment

Changes in atmospheric CO_2 and O_2 concentrations with time are well known (Keeling et al. 1996). The amount of CO_2 released and O_2 consumed during fossil fuel combustion are also recorded (Boden et al. 2010). Outgassing from oceans is also measurable (Plattner et al. 2002). The difference between the atmospheric (light blue) and fossil fuel (red) vectors is made up between the ocean (purple-outgassing and dissolution of CO_2) and the terrestrial biosphere (green).

Oxidative Ratio

Gas exchange studies are critical to understanding where anthropogenic CO_2 is going within the C cycle (Keeling et al. 1996; Severinghaus 1995). Gas exchange rates are controlled by ecosystem oxidative ratio (OR: the net moles of oxygen (O_2) released per mole of CO_2 consumed during net photosynthesis). OR can vary with plant species and ecosystem type (Masiello et al. 2008; Randerson et al. 2006), making understanding how OR shifts with land use change and crop rotations a critical part of understanding the C cycle.

In order to partition anthropogenic CO_2 between the terrestrial biosphere and ocean C reservoirs, the net oxidative ratio of the terrestrial biosphere must be known (OR_{net}). For photosynthesis, OR is the moles of oxygen (O_2) produced per mole of CO_2 consumed (OR_{ab} – a characteristic of the flux of CO_2 from the atmosphere to the biosphere). For decomposition, respiration, and other processes that emit C to the atmosphere, OR is the moles of O_2 consumed per mole of CO_2 released (OR_{ba} – a characteristic of flux of CO_2 from the biosphere to the atmosphere). OR_{net} is the vector sum of these two opposing fluxes weighted by their magnitudes (e.g. net primary production weighted with OR_{ab}; Fig. 4).

Plants record the OR value of photosynthesis in the biochemical signatures of their biomass. OR is a function of the chemistry of biomolecules the plant synthesizes and its N source (Masiello et al. 2008; Randerson et al. 2006). If plants were made entirely of glucose ($C_6H_{12}O_6$), the OR of their biomass would be 1.00, because the fluxes of CO_2 and O_2 are exactly equal in its production. However, variation in plant biochemistry is significant, driving species-specific variations in OR_{ab}.

Two critical assumptions are made about OR in apportionment calculations: 1) OR is constant and 2) OR_{ab} is equal to OR_{ba}.

OR_{net} is assumed constant at 1.10 ± 0.05 for anthropogenic CO_2 apportionment calculations (Fig. 3) (Manning 2001; Prentice et al. 2001; Severinghaus 1995; Manning and Keeling 2006; Keeling et al. 1996), though recent OR estimates are closer to 1.00 (Ciais et al. 2007; Seibt et al. 2004; Stephens et al. 2007). Additionally, an error of 0.05 implies a large uncertainty. Randerson et al. (2006) reported that if estimates of OR_{net} are off by 0.01 over 100 years, 0.1 Pg C yr^{-1} is apportioned into the wrong reservoir. OR values are likely to vary with changes in ecosystem type, nutrient supply, or precipitation, making accurately measuring ecosystem OR critical to constraining a net terrestrial biosphere OR value.

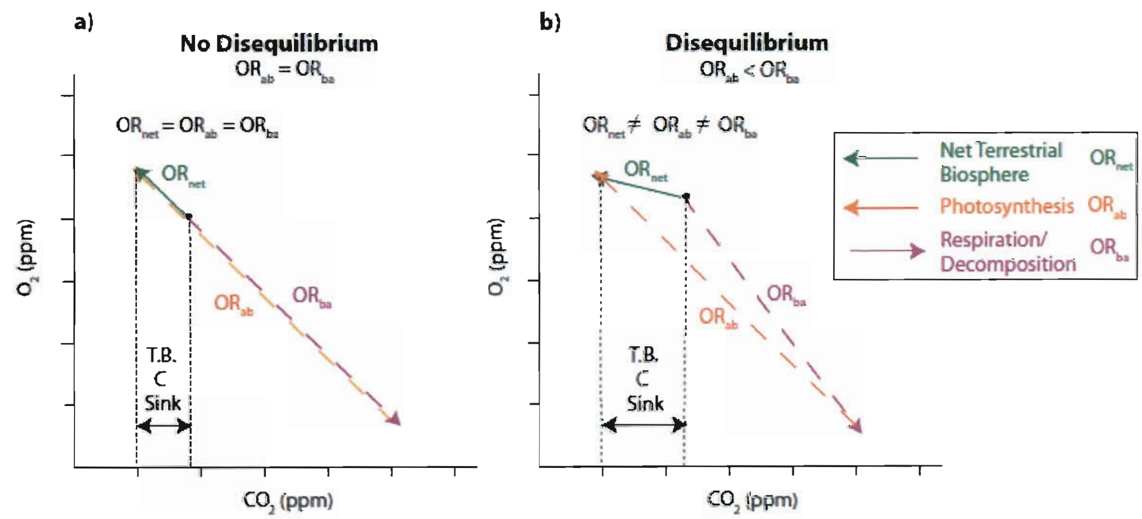

Figure 4. Biospheric Flux OR Impacts the Size of the Net Terrestrial Biosphere C Flux

The angle and size of the net flux to the biosphere (OR_{net}) is determined by the angle of the fluxes to and from the biosphere (OR_{ab} and OR_{ba}, respectively). If the assumption that OR_{ab} is equal to OR_{ba} is incorrect, a disequilibrium exists and the calculated size of the terrestrial biosphere C sink changes. In this schematic the magnitude of the OR_{ab} and OR_{ba} vectors are the same for plots a) and b), but in b) the angle of OR_{ba} is larger. If there is a net global offset between OR_{ab} and OR_{ba}, O_2 and CO_2-based estimates of the size of the terrestrial biosphere C sink increase. Adapted from Randerson et al. (2006).

In apportionment calculations the gas exchange between the atmosphere and the terrestrial biosphere is a summation of processes that remove CO_2 from the atmosphere (photosynthesis) and processes that release CO_2 to the atmosphere (respiration, decomposition, fire). Assuming OR_{ab} equal to OR_{ba} is equivalent to assuming that the stoichiometry associated with these processes are equal but in opposite direction (i.e. photosynthesis releases O_2 while consuming CO_2 in the same ratio that all respiration and decomposition fluxes consume O_2 and release CO_2). It is important to evaluate this assumption carefully, because small net global offsets between OR_{ab} and OR_{ba} can cause large errors in the apportionment of anthropogenic CO_2 between the biosphere and ocean (Randerson et al. 2006). A small net difference between OR_{ab} and OR_{ba} can cause large changes in O_2 and CO_2 flux calculations (Fig. 4; Fig. 5). Randerson et al. (2006) showed that a difference of 0.0175 between OR_{ab} and OR_{ba} is equal to a 1 Pg C yr^{-1} error in C apportionment, equivalent to 16% of global CO_2 emissions in the 1990s (Prentice et al. 2001).

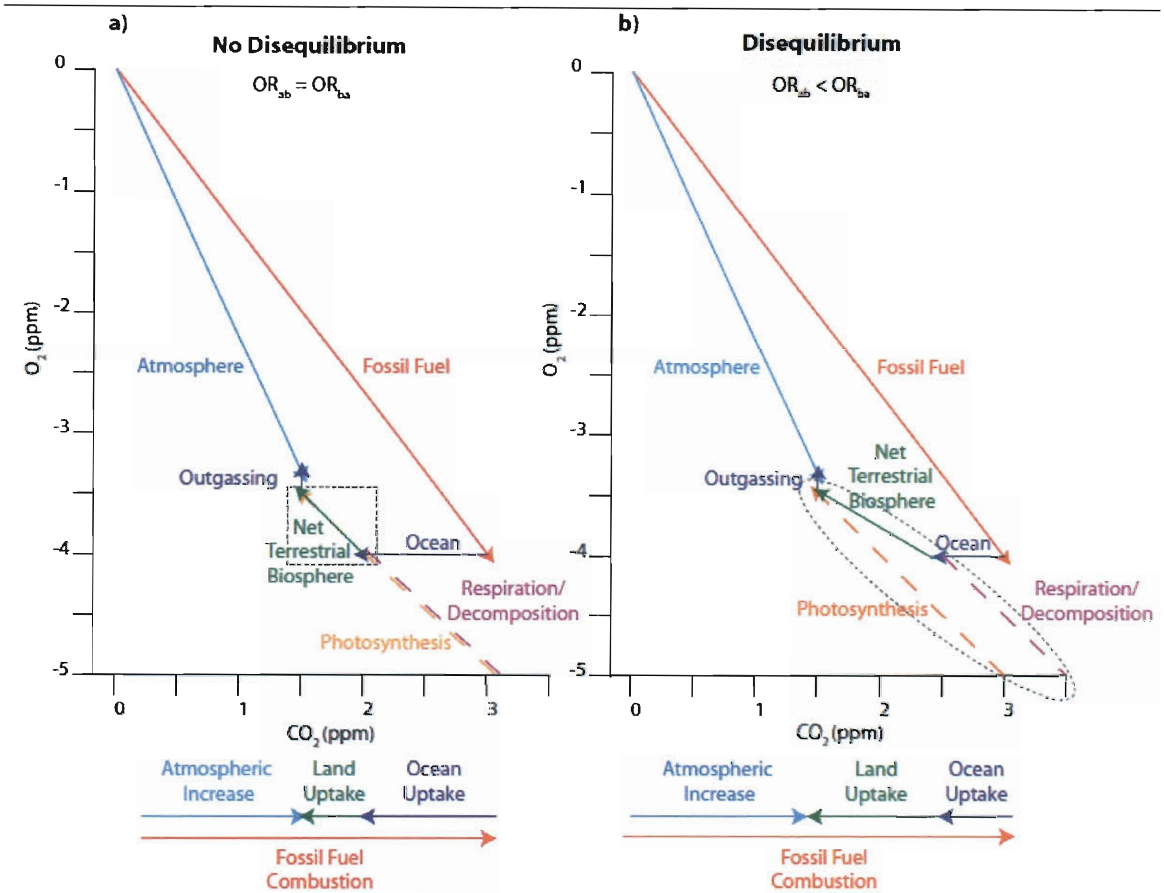

Figure 5. Apportionment Calculation

The vector summations involved in apportionment calculations. This figure shows changes in O_2 and CO_2 over a 10 year period, 1990-1999, where the starting point for each vector represents 1990 and the ending point represents 1999. Axes represent change in concentrations, not actual reservoir values. Figure 5a is the vector diagram when the assumption $OR_{ab}=OR_{ba}$ for the terrestrial biosphere is made (dashed box-see Fig. 4a). Figure 5b is the vector diagram when this assumption is not true (dashed oval-see Fig. 4b). Adapted from Keeling et al. 1996 and Randerson et al. 2006.

Carbon Oxidation State

It is necessary to accurately estimate net OR to constrain the sizes of the terrestrial biosphere and ocean C sinks. However, directly measuring atmosphere O_2 and CO_2 concentrations from gas exchange studies can be difficult (Seibt et al. 2004; Randerson et al. 2006; Ciais et al. 2007; Manning and Keeling 2006). Alternatively, we can estimate OR from the linearly related parameter carbon oxidation state (C_{ox}), which can be directly measured from biomass (Masiello et al. 2008). C_{ox} is a basic property of all organic compounds, describing the bonding environment of the C atoms in a sample. We have developed three techniques to estimate OR from plant biomass: 1) from plant carbon, hydrogen, nitrogen and oxygen (CHNO) measured using elemental analysis (Masiello et al. 2008), 2) from plant heat of combustion using bomb calorimetry and %C measured using elemental analysis (Masiello et al. 2008), and 3) from ^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR), plant C:N ratios, and a molecular mixing model developed by Baldock et al. (2004) (Hockaday et al. 2009).

The Nitrogen Cycle

Humans introduce reactive N (Nr – a form usable by organisms: e.g. nitrate (NO_3^-), ammonium (NH_4^+)) to the environment through fossil fuel combustion, agricultural cultivation of N-fixing plants (e.g. soybeans), and N fertilization (Fig. 6; Galloway et al. 2007; Galloway et al. 2004). Such activities have almost doubled the rate of Nr introduced into the environment (Vitousek et al. 1997). Galloway et al. (2004) estimated that in the 1990s anthropogenic sources of Nr accounted for ~40% of Nr production globally, a significant increase from ~6% in 1860. This is primarily due to the invention of the Haber-Bosch process (i.e. N fertilization). Fertilizer makes up 90% of the United States' ammonia, which is primarily used by the agricultural industry (Galloway et al. 2004; 2007; Kramer 2007).

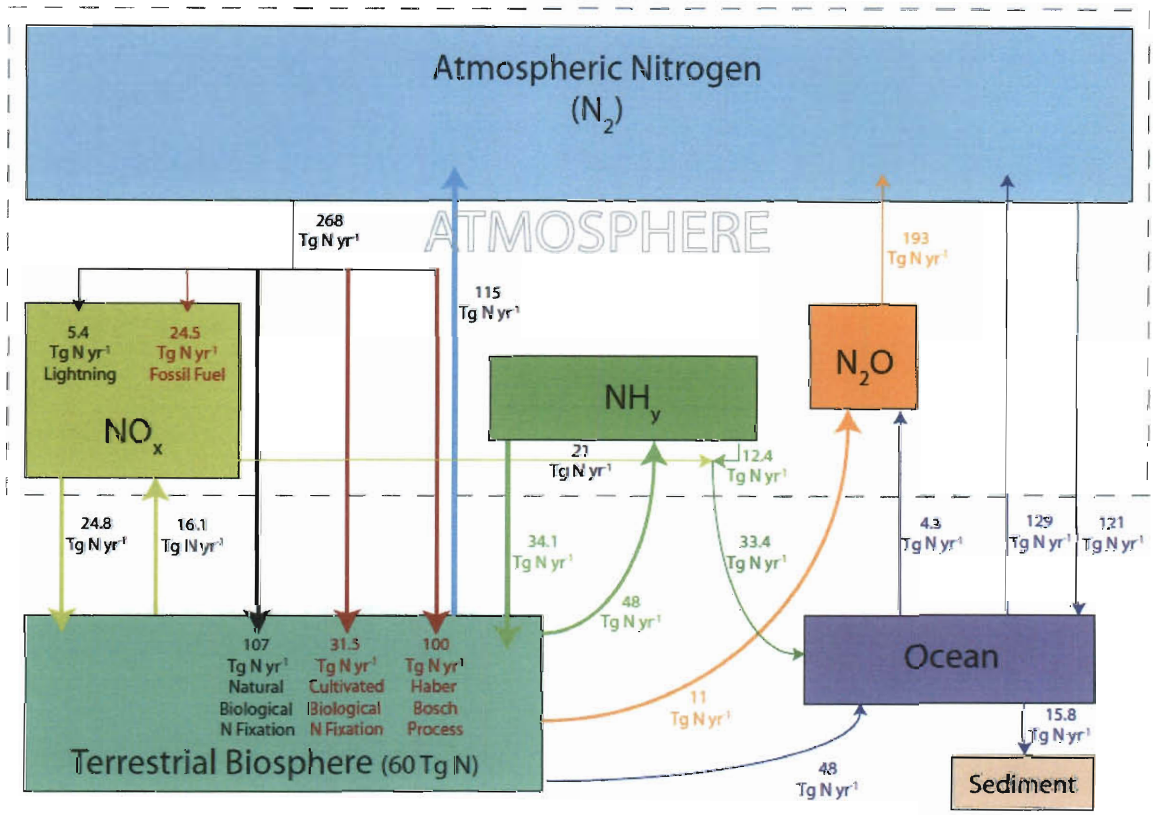

Figure 6. The Nitrogen Cycle during the 1990s

Adapted from Galloway et al. (2004). Anthropogenic sources of N to the terrestrial biosphere (cultivation of N-fixing crops, and N fertilizer) convert atmospheric nitrogen (N_2) into a usable for of N. In the 1990s, anthropogenic sources of N (107 Tg N yr^{-1}) to the terrestrial biosphere were larger than natural N fixation sources (131.5 Tg N yr^{-1}).

Nitrogen Fertilizer

Application of N fertilizer has been shown to increase crop yield in nutrient depleted ecosystems (e.g. McSwiney and Robertson 2005). In addition, plant biochemical shifts in response to fertilizer have been observed using biological assays and near-infrared spectroscopy, where a typical response is increased protein and decreased carbohydrate (Zhang et al. 1993). Shifts in biomass allocation to different plant tissues (grain, leaves, stems, and roots) can also cause shifts in plant biochemical stocks since plant tissues each have a specific biochemical profile (Poorter and Bergkotte 1992; Poorter and Nagel 2000).

N fertilization has major environmental impacts. There are serious negative consequences to excessive N fertilization (Carpenter et al. 1998), such as nitrate (NO_3^-) runoff (Bergstrom and Brink 1986; Power et al. 2000). Excessive use of N fertilizers is the cause of the current hypoxic 'dead zone' in the Gulf of Mexico (Burkart and James 1999; Turner et al. 2008; Rabalais et al. 2007). Nitrate runoff into groundwater supplies has been linked to a number of health problems including, but not limited to: Alzheimer's disease, oral cancer, multiple sclerosis, and Non-Hodgkin's lymphoma (Rao and Puttanna 2006). Furthermore, the use of synthetic fertilizers contributes to greenhouse gas emissions through carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions during production (Wood and Cowie 2004). N_2O is a potent greenhouse gas with a global warming potential (GWP) of 310 (Forster et al. 2007). N_2O emissions from soils increase nonlinearly in response to increased N fertilizer applications (McSwiney and Robertson 2005). Whether a crop is to be used for food or for fuel, it is critical to understand how to maximize crop yield while minimizing fertilizer application and energy consumption in order to mitigate these environmental problems.

Agricultural Ecosystems

Agricultural ecosystems make up between 34-40% of the terrestrial biosphere, challenging forests for the largest ecosystem type globally (Leff et al. 2004; Ramankutty and Foley 1999b; Foley et al. 2005). Increasing population projections have created concerns about food, water, land, and energy shortages (Spiertz 2010). Agriculture ecosystems are major consumers of water, land, and energy and are critical to the food and, in recent years, the energy industries. The agricultural industry focuses on manipulating land for production, which has significant environmental impacts. Land use change has led to ~15 million km^2 and 31.5 million km^2 of natural vegetation being converted into cropland and pasture, respectively (Ramankutty et al. 2008). Conversion of natural vegetation to agriculture, and agricultural management techniques (e.g. tillage, pesticides, herbicides, fertilizer, irrigation, cover and catch crops, etc.) impact the environment, leading to uncertainty about what will drive changes in agriculture in the future and how this will affect the environment (Hazell and Wood 2008). Environmental impacts on local- to regional-scales are well understood, but global-scale impacts of agriculture on the Earth System remain challenging to quantify.

Agricultural Crops

The top five world crops are wheat (22%), corn (13%), rice (11%), barley (9%), and soybeans (5%) (Leff et al. 2004). Since the early 1960s, corn, soybean, and wheat have accounted for the most acreage in planted cropland in the United States (≥64%; ≥80% since 1990; NASS 2010; USDA 2006). Before then, corn, wheat, and oats were the top three crops in the U.S. (NASS 2010). Since the 1990s corn and soybean acreage has been increasing, while wheat acreage has been decreasing (NASS 2010; USDA 2010). In 2010, corn, soybean, and wheat accounted for 35%, 31%, and 21% of total planted acreage in the U.S., making the study of these crops critical to estimating a U.S. agriculture OR (Fig. 7; Chapter 2; NASS 2010; USDA 2006).

Soybean is a major U.S. crop (31% of cropland in 2010; 5% of world croplands) and the most important legume (N-fixing) crop (NASS 2010; Leff et al. 2004). Soybean represents half of global legume crops and 77% of the total N fixed by crop legumes (Herridge et al. 2008). Major uses for soybean include food (soy, soy milk, etc), feedstock (its high protein is useful in animal feed), and energy feedstock (biodiesel).

Wheat, on the other hand, is primarily used as a food crop. Wheat is the most prevalent world crop (22%), while the third most abundance crop in the U.S., 21% (Leff et al. 2004; NASS 2010). New developments in the biofuels industry may lead to wheat straw being used as a feedstock in cellulosic ethanol production.

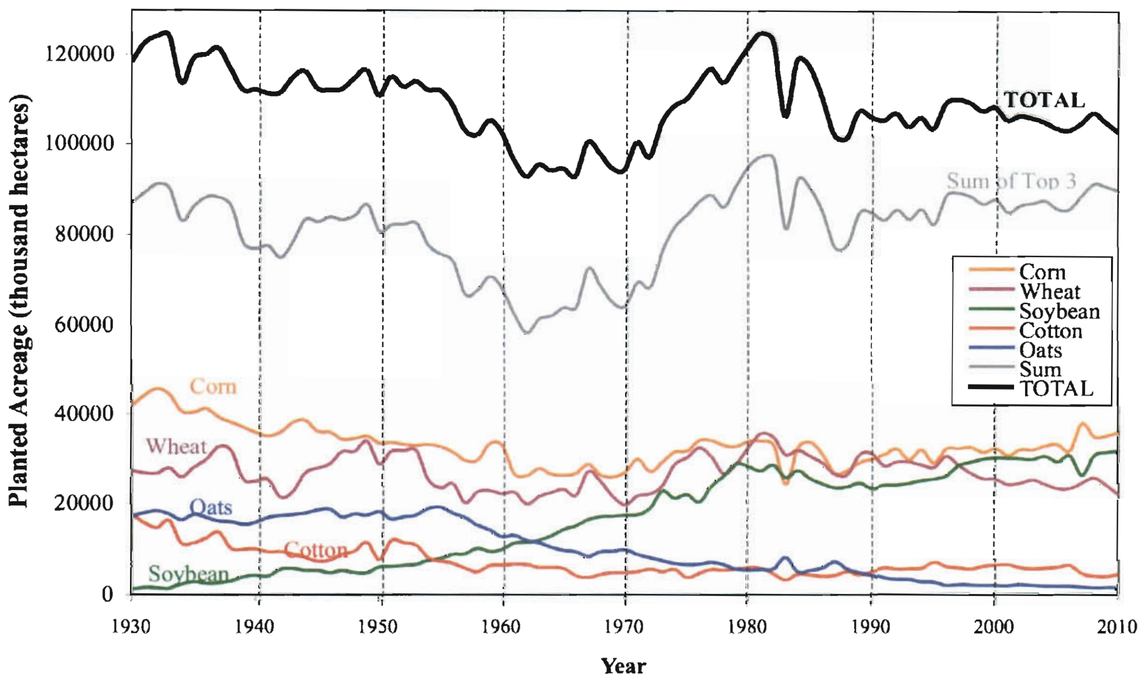

Figure 7. U.S. Planted Crop Acreage from 1930 to 2010

U.S. crop planted acreage (thousand hectares) for corn, soybean, wheat, cotton, oats, the sum of the top 3 crops for that year, and the total planted crop acreage for that year. The top 3 crops represents between 65%-87% of total U.S. crop planted acreage depending on the year (NASS 2010).

Corn is the major crop for the U.S. (35% of cropland in 2010; NASS 2010) and the world (13%; Leff et al. 2004). In 2006, corn acreage was projected to increase over the following ten years due to increases in export and bioenergy production (USDA 2006). The latest USDA Agricultural Projections predict corn acreage to plateau between 35.6-36.4 million hectares after 2012 (USDA 2010). Despite only slight variations in corn planted acreage over the past 80 years (Fig. 7), advances in agricultural technologies and management techniques has led to significant increases in yield (433% from 1930 to present; Fig. 8). N fertilization is a critical part of this increase in productivity, particularly in corn ecosystems. In the United States almost every hectare of corn is treated with N (ARMS 2005). This makes corn agricultural ecosystems ideal field sites for the study of the global scale effects of agricultural manipulations of the C and N cycles.

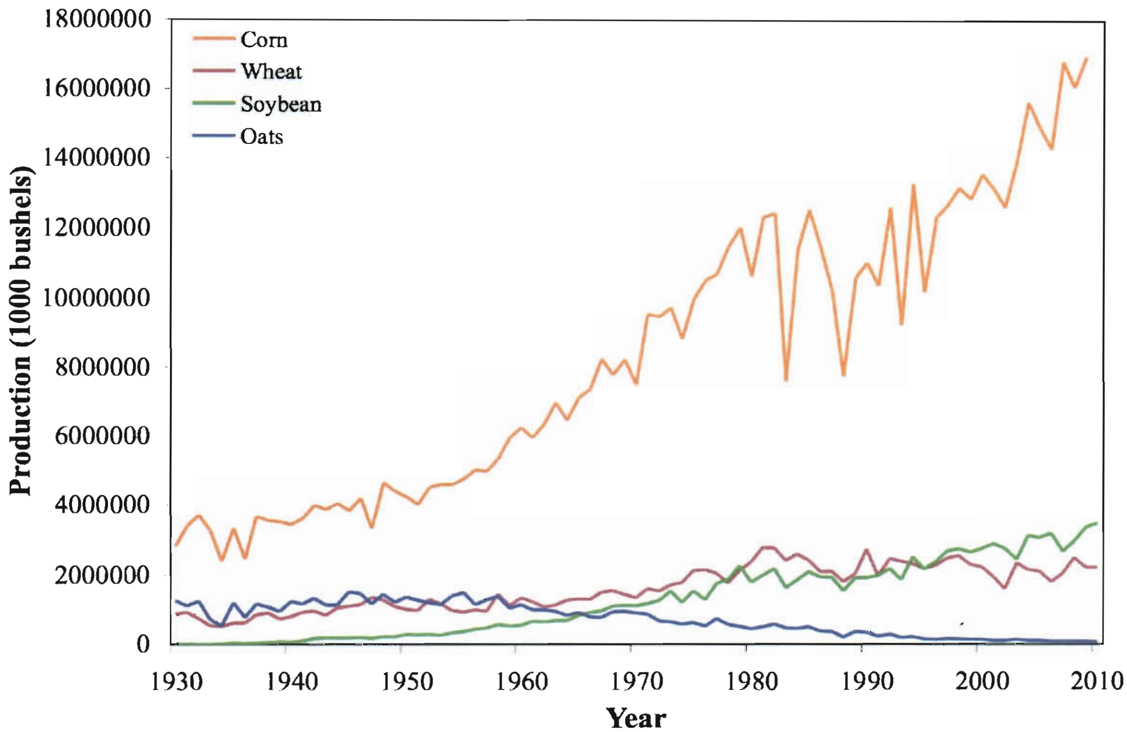

Figure 8. U.S. Crop Yields from 1930 to 2010

U.S. production of the top four crops (corn, wheat, soybean, and oats), in thousand bushels, from 1930 to present (NASS 2010). Though the largest change in corn acreage is no more than 42% (decrease in acreage from 1930 to 1962; Fig. 7), corn production (for grain and silage) has increased by 433% from 1930 to present.

Agriculture and the Biofuels Industry

Growing concerns over greenhouse gas emissions, climate change, and rising oil prices have increased biofuel demand (Solomon et al. 2007). Biofuels are fuels derived from biomass and include: bioethanol, biodiesel, vegetable oils, bio-gas, bio-oil and biochar (Demirbas 2008). The agricultural industry is critical to the future of the biofuels industry since it provides the feedstocks for all these biofuels. The two biofuels at the forefront of the industry are ethanol derived from corn grain, known as corn grain ethanol and ethanol derived from lignocellulosic materials (e.g. corn stover), known as cellulosic ethanol (McKendry 2002; Sanchez and Cardona 2008).

Grain Ethanol

Corn grain ethanol, a first-generation biofuel, is the main form of ethanol currently being produced (Bothast and Schlicher 2005; Service 2007). Corn grain ethanol is beneficial because it produces more energy than it takes to create it (Hill et al. 2006), is biodegradable, and decreases automotive carbon monoxide emissions due to its higher oxygen content (DiPardo 2000; Bothast and Schlicher 2005). However, approximately one sixth of the global population, or 1.02 billion people, is undernourished (FAO 2009), making corn grain ethanol production ethically questionable since it uses corn grain as a fuel source rather than a food source (Pimentel et al. 2009). Increasing demand for corn grain ethanol is leading to increased corn acreage (19% increase in acreage in the United States from 2006 to 2007), decreased crop diversity (Landis et al. 2007), increased soil erosion, and increased use of N fertilizer, pesticides, and herbicides (Pimentel et al. 2009; NASS 2005a; McLaughlin and Walsh 1998; Patzek 2004).

Cellulosic Ethanol

One promising advance in the biofuels industry is cellulosic ethanol production. The use of non-grain feedstocks (i.e. crop residues), rather than grain, for ethanol production would prevent the biofuels and food industries from competing with each other for commodities, and reduce the risk of further land conversion to agriculture to meet the demand from both industries (Pimentel et al. 2009; Ugarte et al. 2006; Service 2007). Cellulosic ethanol converts the carbohydrates (i.e. cellulose) in plant feedstocks to sugars, which can then be converted into ethanol (Solomon et al. 2007).

Cellulosic ethanol production has challenges to overcome before becoming an economically viable alternative fuel, including challenges related to plant lignin content. In cellulosic ethanol production, the cellulosic material in the feedstock is degraded into a sugar solution, which microbial fermentation then converts into cellulosic ethanol (Sanchez and Cardona 2008). Lignin is extremely difficult for enzymes and microbes to degrade and its presence slows down the conversion of cellulose to fuel (Hamelinck et al. 2005; McKendry 2002). To achieve the highest efficiency of conversion, lignin must be physically or chemically removed from biomass before fermentation (Sanchez and Cardona 2008; Weng et al. 2008). Several approaches have been taken to address the lignin issue, including improving the chemical processing the biomass undergoes at the ethanol plant (Sun and Cheng 2002; Wyman 2007), genetically altering enzymes and microbes to breakdown lignin (Zhang et al. 1995), and genetically engineering plants to contain less lignin (Sticklen 2008).

To make the cellulosic biofuels industry both economically and environmentally viable, we need to understand what sustainable agricultural management techniques will maximize yields, while minimizing environmental impacts when cropping for fuels. Emissions of fossil fuel-derived CO_2 and N_2O from biofuel crop systems, can significantly reduce the climate benefits associated with the use of biofuels (Hill et al. 2009; Robertson et al. 2008). Practices that improve sustainability (e.g. the use of a cover crop, which reduces soil erosion and in some cases alters N availability) can prolong crop grain and crop residue yields over the long-term (Ugarte et al. 2006). Other practices, like N fertilization, that affect crop biochemistry (i.e. the percent carbohydrate, protein, lignin, and lipid) will affect not only total biochemical yields but also the efficiency with which the feedstock is processed into ethanol. In addition, the agricultural industry needs to select appropriate feedstocks for biofuel production (feedstocks that have suitable biochemical signatures) and use management techniques to optimize feedstock biochemistry (i.e. high carbohydrate, low lignin concentrations; Sanchez and Cardona 2008).

It should be noted that the agricultural industry is a business first and foremost. If sustainable agriculture practices do not maintain or increase profits, it is unlikely they will be widely implemented. Therefore, when making recommendations on which agricultural management techniques produce higher quality crops or minimize environmental impacts, it is also essential to consider costs, cost-efficiency, and, where possible, profit margins.

Agricultural Management Techniques

The agricultural industry has global scale environmental impacts, leading to increased efforts to develop environmentally sustainable management techniques. The primary goal of most agricultural management techniques is to increase crop yield. Some techniques used for this include herbicides, pesticides, fertilizer, and irrigation. Other techniques are used to improve agricultural sustainability (cover crops, catch crops, no-till, organic practices, etc.). Practices that improve sustainability can prolong crop grain and crop residue yields over the long-term (Ugarte et al. 2006).

Cover Crop

The use of a cover crop can have both environmental and economic benefits. A cover crop can reduce soil erosion, increase soil N availability (e.g. legume cover crops), reduce pests and disease, increase crop yield, and potentially be used as a secondary cash crop (as reviewed in Snapp et al. 2005). Some cover crops are used as catch crops, "catching" or immobilizing soil N by removing it from the soil and storing it in their biomass (McSwiney et al. 2010). When this crop is tilled into the soil before planting, it acts as a slow-release fertilizer as it decomposes.

Agriculture and the Carbon and Nitrogen Cycles

Agriculture plays major roles in both the C and N cycles (Fig. 9). The agricultural industry focuses on manipulating land for production, which can impact the C cycle. Land use change has led to ~15 million km^2 and 31.5 million km^2 of natural vegetation being converted into cropland and pasture, respectively (Ramankutty et al. 2008). Land use change, soil tilling, use of farm machinery, and fertilizer and pesticide production are all agricultural anthropogenic sources of CO_2 to the atmosphere (Robertson and Grace 2004; Houghton and Goodale 2004). In addition cropping has led increased soil erosion, and decreased soil organic C accumulation (Grandy and Robertson 2007; Ortega et al. 2002; Tiessen et al. 1994), However, the agricultural industry has the potential to mitigate anthropogenic CO_2 emissions through sustainable agricultural practices (e.g. no-till, cover crop) that promote soil carbon sequestration (Robertson et al. 2000; Robertson and Grace 2004; Six et al. 2000). Agricultural ecosystems cropped for biofuels also have the potential to mitigate greenhouse gas emissions by replacing fossil fuels (Robertson et al. 2008). Application of N fertilizer can lead to N_2O emissions and nitrate leaching (McSwiney and Robertson 2005; Bergstrom and Brink 1986; Power et al. 2000). N fertilizer can also impact C cycle gas exchange fluxes through altering decomposition rates and soil respiration of CO_2 (Singh and Gupta 1977).

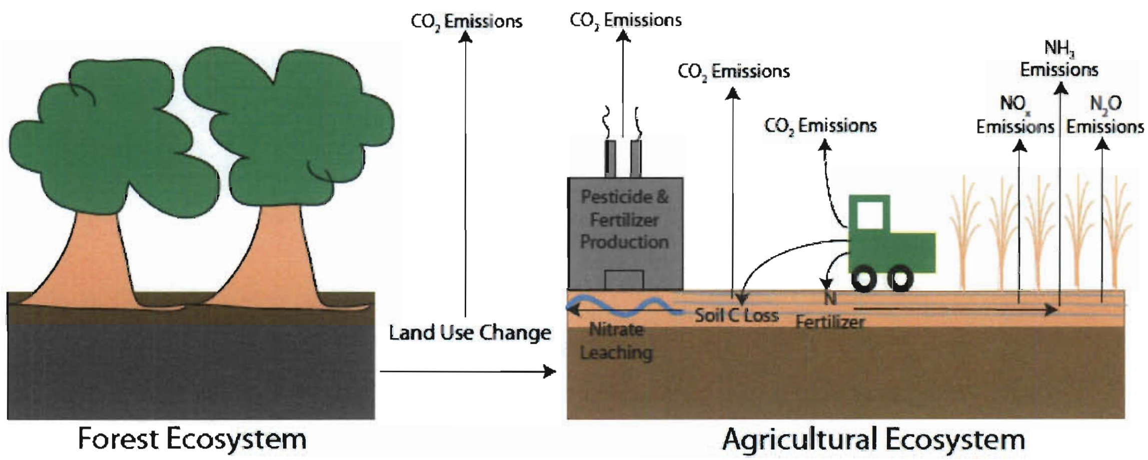

Figure 9. Agricultural Impacts on the Carbon and Nitrogen Cycles

Agriculture impacts the C cycle primarily through CO_2 emissions from land use change, fertilizer and pesticide production, machinery, and soil C loss due to tillage. Agriculture impacts the N cycle through N-fixing crops and N fertilizer applications, which lead to nitrate leaching and emissions of NO_x, NH_3, and N_2O to the atmosphere.

My thesis results and conclusions are presented in the following four chapters. In Chapter 2, I explore the concept of OR, which is critical to accurate apportionment of anthropogenic CO_2 between C sinks (i.e. the terrestrial biosphere and the ocean). I measure ecosystem OR values for three major U.S. and world crops (soybean, wheat, and corn) as well as assess the impact of management techniques (N fertilization and cover crop) on OR. Chapter 3 discusses the biochemical stocks of corn over an N fertilization gradient and the implications of these results for the biofuels industry. I observe a nonlinear increase in corn grain carbohydrate and protein yields, plateauing after 67 kg N ha^{-1}. Crop residue carbohydrate yields increase slightly (25% with 202 kg N ha^{-1}), while lignin increases 41%, thereby producing a lower quality cellulosic ethanol feedstock at high fertilization rates. Chapter 4 expands on this work by studying how the addition of a winter wheat cover crop to the N fertilizer gradient affects corn biochemical stocks. I also developed a cost-assessment model to determine which agricultural management technique is the most cost-effective depending on the end product (grain for food, grain for ethanol, or crop residue for cellulosic ethanol). Chapter 5 summarizes my results and general conclusions.

CHAPTER 2

Controls on the Oxidative Ratio of Agricultural Ecosystems

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In Preparation for

Global Biogeochemical Cycles

Abstract

Accurately and precisely constraining ecosystem oxidative ratio (OR) is necessary to assess the sizes of the terrestrial biosphere and ocean C sinks, as well as the rate at which they are taking up anthropogenic carbon dioxide. The Intergovernmental Panel on Climate Change (IPCC)-used global OR estimate in apportionment calculations is 1.10 ± 0.05. Techniques currently used to estimate OR values are prone to error, which can lead to large errors in estimations of the sizes of C sinks. An error of ±0.05 OR units is equivalent to an error of 0.5 Pg C yr^{-1} or 50 Pg C over 100 years. We have developed several methods for estimating OR from biomass chemistry that are more accurate and precise. To better constrain biospheric OR, measurements need to be made across a range of ecosystems. Agriculture comprises approximately 34% of the terrestrial biosphere surface area, making constraining its OR a critical first step in constraining the terrestrial biosphere's OR. Here we analyze the top three crops in the U.S. (soybean, corn, and wheat) and show significant differences between the OR of legumes versus grass crops. We make a preliminary estimate a 2003-2005 average U.S. agriculture OR value of 1.060 ± 0.003, an increase from 1.040 in the 1930s. We additionally test the effect of nitrogen fertilization on corn ecosystem OR and observe no detectable changes. Finally, we assess the accuracy of the assumption that the OR values of photosynthesis and organic matter decomposition are equal. We show for a corn monoculture ecosystem, that while these values are equal within error on annual timescales, the process of soil organic matter formation leads to offsets on longer timescales. These results imply that ecosystem OR is not constant over time or space.

Introduction

Anthropogenic CO_2 Emissions

It is unclear how increasing atmospheric carbon dioxide (CO_2) will affect ecosystems, both in the direction and magnitude of the impact. Increasing atmospheric CO_2 is currently decreasing ocean pH, (Ruttimann 2006; Orr et al. 2005), altering terrestrial ecosystem composition (Polley et al. 2003; Polley et al. 2002), and is likely altering plant growth patterns (e.g. Hamilton et al. 2002; Norby et al. 2004), and thereby the food web (Emmerson et al. 2005). Increased atmospheric temperatures due to CO_2-driven climate change, are also predicted to change our environment by reducing polar ice caps, increasing sea level, changing shorelines, and shifting ecosystem-latitudinal extent (Prentice et al. 2001; EPA 2006a). These changes are expected to affect society and human health through disease vector movement, population relocation near shorelines, increased mortality rates during extreme heat events, and increased famines (EPA 2006b). The accuracy of these predictions depends, in part, on how well we understand the carbon (C) cycle and the fate of anthropogenic CO_2 in the environment.

Anthropogenic CO_2 Apportionment

It has been observed that the increased emissions of CO_2 to the atmosphere are being partially compensated for by two C sinks: one located in the terrestrial biosphere and another in the ocean (Tans et al. 1990; Keeling et al. 1996; Manning and Keeling 2006). The approximate sizes of these sinks can be calculated using atmospheric oxygen (O_2) and CO_2 time series data (Keeling and Shertz 1992; Keeling et al. 1996; Bender et al. 1998; Battle et al. 2000; Manning 2001; Bender et al. 2005; Manning and Keeling 2006).

Understanding the time-varying fate of anthropogenic CO_2 is important for several reasons. First, this information allows observation of how the terrestrial biosphere and ocean C fluxes respond to increasing anthropogenic CO_2 emissions, helping determine if the terrestrial biosphere and oceans are increasing, maintaining, or decreasing their C uptake rates (Le Quere et al. 2009; Raupach et al. 2008). Second, a better understanding of the terrestrial and ocean C uptake rates and their mechanisms will help develop effective C management strategies; for example, improving land management (Smith 2004), greening the oceans (Bakker 2004) or protecting vulnerable C reservoirs (e.g. boreal soil C pools – Schuur et al. 2009). Lastly, understanding the partitioning of anthropogenic CO_2 between reservoirs allows for more dependable climate forecasts (Manning and Keeling 2006).

To calculate the partitioning of C sinks between the ocean and land, the net oxidative ratio of the terrestrial biosphere (OR_{net}) must be known. In general, OR relates changes in O_2 to changes in CO_2 for processes such as photosynthesis, respiration, fire, and fossil fuel combustion (Eqn. 1).

$$\frac{dO_2}{dt} = -OR \cdot \frac{dCO_2}{dt} \qquad \text{Eqn. 1}$$

OR_{net} is associated with the net flux of such processes occurring between the terrestrial biosphere and the atmosphere (e.g. photosynthesis, decomposition, respiration). For photosynthesis, OR is the moles of O_2 produced per mole of CO_2 consumed (OR_{ab} – a characteristic of the flux of CO_2 from the atmosphere to the biosphere). For decomposition, respiration, and other processes that return C to the atmosphere, OR is the moles of O_2 consumed per mole of CO_2 released (OR_{ba} – a characteristic of flux of CO_2 from the biosphere to the atmosphere). The net flux between the terrestrial biosphere and the atmosphere ($F_{TB} = \frac{dCO_2}{dt}_{TB}$) is related to these processes via Eqn. 2.

$$-OR_{net} \cdot F_{TB} = (-OR_{ab} \cdot F_{ab}) + (-OR_{ba} \cdot F_{ba}) \qquad \text{Eqn. 2}$$

It should be noted that OR values are always positive and the sign associated with the fluxes between reservoirs ($F = \frac{dCO_2}{dt}$; e.g. $F_{FF} = \frac{dCO_2}{dt}_{FF}$) indicate its direction. F_{ab} is the magnitude of the flux of C from the atmosphere to the biosphere (net primary production). Since this is a draw down of C, this magnitude is negative. Fluxes that introduce C to the atmosphere (F_{ba}, or fossil fuel combustion - $\frac{dCO_2}{dt}_{FF}$) are positive. OR_{net} is the vector sum of these two opposing fluxes weighted by their magnitudes (Eqn. 3; Fig. 10).

$$OR_{net} = \frac{OR_{ab} \cdot F_{ab} - OR_{ba} \cdot F_{ba}}{F_{ab} + F_{ba}} \qquad \text{Eqn. 3}$$

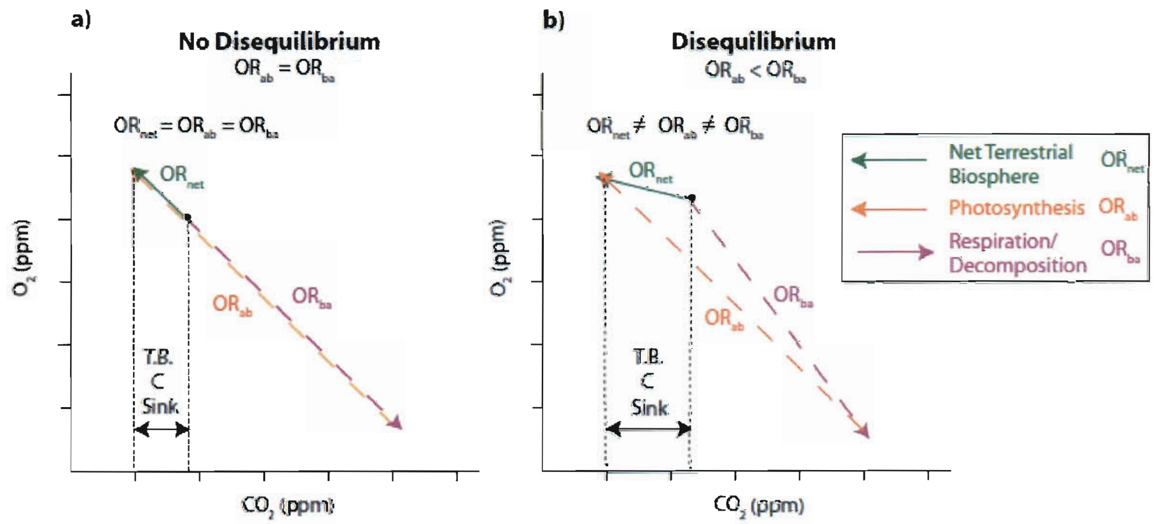

Figure 10. Biospheric Flux OR Impacts the Size of the Net Terrestrial Biosphere C Flux

The angle and size of the net flux to the biosphere (OR_{net}) is determined by the angle of the fluxes to and from the biosphere (OR_{ab} and OR_{ba}, respectively). If the assumption that OR_{ab} is equal to OR_{ba} is incorrect, a disequilibrium exists and the calculated size of the terrestrial biosphere C sink changes. In this schematic the magnitude of the OR_{ab} and OR_{ba} vectors are the same for plots a) and b), but in b) the angle of OR_{ba} is larger. If there is a net global offset between OR_{ab} and OR_{ba}, O_2 and CO_2-based estimates of the size of the terrestrial biosphere C sink increase. Adapted from Randerson et al. (2006).

The OR value of photosynthesis is recorded in the chemistry of a plant's biomass, and is primarily a function of the chemistry of biomolecules the plant synthesizes and secondarily is a function of the plant's nitrogen (N) source (Masiello et al. 2008; Randerson et al. 2006). The oxygen taken up as water (H_2O) and CO_2 through photosynthesis is either incorporated into plant biomass or returned to the atmosphere as O_2. Variations in plant biochemistry are significant (e.g. Poorter and Bergkotte 1992; Masiello et al. 2008) and lead to species-specific variations in OR_{ab}. If plants were made entirely of cellulose (a polymer of $C_6H_{12}O_6$), the OR of their biomass would be 1.00, because the fluxes of CO_2 and O_2 are exactly equal in the production of this biomolecule. During the synthesis of lipids and other compounds containing reduced forms of C, plants return more O_2 to the atmosphere compared to the amount returned during synthesis of carbohydrates. For example, oleic acid, the main lipid present in olive oil, requires very little oxygen for its molecular construction ($C_{18}H_{34}O_2$) and this compound's synthesis returns large O_2 fluxes to the atmosphere ($OR_{ab} = 1.42$). Conversely, little O_2 is returned to the atmosphere during the synthesis of oxidized biomolecules like oxalic acid ($C_2H_2O_4$; $OR_{ab} = 0.25$). The OR of the average plant lipid is 1.37; of lignin and protein, 1.13; of phenol, 1.05; and of organic acid, 0.68 (Masiello et al. 2008; Randerson et al. 2006). Carbohydrate and charcoal produced from biomass burning share an OR of 1.00 (Masiello et al. 2008; Randerson et al. 2006).

N sources may also provide varying amounts of oxygen to plants (nitrate (NO_3^-) brings oxygen, while ammonium (NH_4^+) does not); therefore, a complete understanding of an ecosystem's OR requires some understanding of N sources as well (Masiello et al. 2008; Ciais et al. 2007; Randerson et al. 2006). Shifting N sources from NO_3^- to NH_4^+

will alter ecosystem OR by changing O_2 fluxes (Ciais et al. 2007). Although plant uptake of sulfur and phosphorous also supplies O_2 (sulfate (SO_4^{3-}) and phosphate (PO_4^{3-}), respectively), they do not bring enough to significantly alter ecosystem OR (< 0.0002 units, which is smaller than measurement error; Hockaday et al. 2009).

Variations in plant nutrient status can change plant biochemistry, for example, by increasing the protein yield in grain crops (Gallagher et al. In Review). Variations in plant biochemistry between species can be expected to result in ecosystems characterized by different OR values. In this paper we explore the effects of nutrient status and crop ecosystem species composition on OR values.

Finally, we address two implicit, but critical assumptions made about OR in C sink partitioning calculations: 1) that OR_{net} is constant over space and time, and 2) that OR_{ab} is equal to OR_{ba}, but see Severinghaus (1995) (Randerson et al. 2006). Although we recognize other potential sources of uncertainty in OR, including CO_2 and climate-driven shifts in plant biochemistry and land use change, these are not the topic of this paper.

Assumption 1: OR_{net} is constant over time and space.

For anthropogenic CO_2 calculations (see Table 1; Fig. 11; Eqns. 1-7), such as those made in the Third Assessment Report, OR_{net} is assumed constant at 1.10 ± 0.05 (Manning 2001; Prentice et al. 2001; Manning and Keeling 2006; Severinghaus 1995; Keeling et al. 1996). The value of 1.10 and its constancy have come into question recently, with new OR estimates closer to 1.00 (Ciais et al. 2007; Seibt et al. 2004; Stephens et al. 2007). Additionally, an error of 0.05 implies a large uncertainty. Randerson et al. (2006) reported that if estimates of OR_{net} are off by 0.01 over 100 years, 0.1 Pg C yr^{-1} is apportioned into the wrong reservoir. Hence, the error surrounding the current OR value used translates to a $\pm$ 0.5 Pg C yr^{-1}, or ±20-100% of the terrestrial biosphere and ocean C uptake rates, which have been estimated to range from 0.5 – 2.5 Pg C yr^{-1} (Manning 2001; Manning and Keeling 2006; Le Quere et al. 2009). Just as plant biochemistry varies with a number of environmental factors, OR values are likely to vary with some combination of changes in ecosystem type, nutrient supply, or precipitation.

Table 1. Apportionment Calculation Terms, Equations, and Values

Equations, definitions and values of terms used to calculate changes in O_2 and CO_2 with time for the atmosphere, biosphere, and ocean reservoirs as well as O_2 consumed and CO_2 released by fossil fuel combustion. Subscript definitions: $_{Atmo}$: Atmosphere; $_{FF}$: Fossil Fuel; $_{TB}$: Terrestrial Biosphere; $_{Oc}$: Ocean; $_{ab}$: atmosphere to biosphere flux; $_{ba}$: biosphere to atmosphere flux. [A](Manning and Keeling 2006); [B](Keeling et al. 2005); [C](Boden et al. 2010); [D](Levitus et al. 2000; Plattner et al. 2002); N/A: not applicable

Term	Formula	Value	Definition
$\frac{dO_2}{dt}_{Atmo}$	$= \frac{dO_2}{dt}_{FF} + \frac{dO_2}{dt}_{TB} + \frac{dO_2}{dt}_{Oc}$	-13.72 per meg yr^{-1} [A]	The decrease in atmospheric O_2 concentrations with time
$\frac{dCO_2}{dt}_{Atmo}$	$= \frac{dCO_2}{dt}_{FF} + \frac{dCO_2}{dt}_{TB} + \frac{dCO_2}{dt}_{Oc}$	1.39 ppm yr^{-1} [B]	The increase in atmospheric CO_2 concentrations with time
$\frac{dO_2}{dt}_{FF}$	$= OR_{FF} \cdot \frac{dCO_2}{dt}_{FF}$	-15.97 per meg yr^{-1} [C]	The amount of O_2 consumed by fossil fuel combustion with time
$\frac{dO_2}{dt}_{TB}$	$= OR_{net} \cdot \frac{dCO_2}{dt}_{TB}$	N/A	The amount of O_2 released by net photosynthesis in the terrestrial biosphere with time
$\frac{dO_2}{dt}_{Oc}$		1.93 per meg yr^{-1} [D]	The amount of O_2 released from the oceans due to outgassing with time
$\frac{dCO_2}{dt}_{FF}$		2.99 ppm yr^{-1} [C]	The amount of CO_2 released by fossil fuel combustion with time
$\frac{dCO_2}{dt}_{TB}$	$= \left[\frac{1}{OR_{net}}\right] \cdot \left[\frac{dO_2}{dt}_{Atmo} - OR_{FF} \cdot \frac{dCO_2}{dt}_{FF} - \frac{dO_2}{dt}_{Oc}\right]$	Unk.	The amount of CO_2 consumed by net photosynthesis in the terrestrial biosphere with time
$\frac{dCO_2}{dt}_{Oc}$	$= \frac{dCO_2}{dt}_{Atmo} - \frac{dCO_2}{dt}_{FF} - \frac{dCO_2}{dt}_{TB}$	Unk.	The amount of CO_2 dissolved by the oceans with time
OR_{FF}	Gas Fuel=1.95; Liquid Fuel=1.44; Solid Fuel=1.17; Cement=0.00; Gas Flaring=1.98[5]	1.393	Avg. moles of O_2 consumed per mole of CO_2 released during fossil fuel combustion
OR_{net}	$= \frac{OR_{ab} \cdot F_{ab} - OR_{ba} \cdot F_{ba}}{F_{ab} + F_{ba}}$	1.10	Moles of O_2 released per mole of CO_2 consumed by net photosynthesis

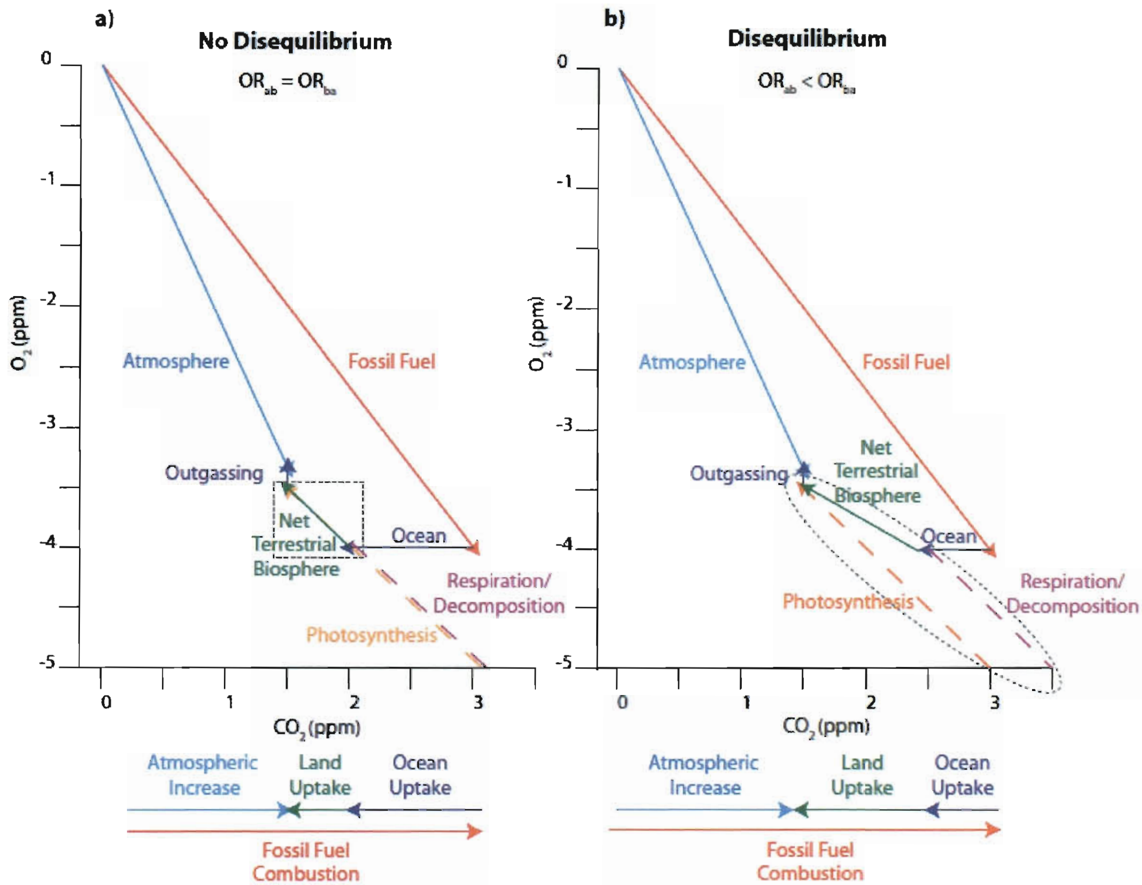

Figure 11. Apportionment Calculation

The vector summations involved in apportionment calculations. This figure shows changes in O_2 and CO_2 over a 10 year period, 1990-1999, where the starting point for each vector represents 1990 and the ending point represents 1999. Axes represent change in concentrations, not actual reservoir values. Figure 11a is the vector diagram when the assumption OR_{ab}=OR_{ba} for the terrestrial biosphere is made (dashed box-see Fig. 10a). Figure 11b is the vector diagram when this assumption is not true (dashed oval-see Fig. 10b). Adapted from Keeling et al. 1996 and Randerson et al. 2006.

Agricultural Management May Drive OR Shifts

One factor that has the potential to affect global OR is shifting N supply. Humans introduce N to the environment through fossil fuel combustion, agricultural cultivation of N-fixing plants (e.g. soybeans), and N fertilization (Galloway et al. 2007). Such activities have almost doubled the rate of reactive nitrogen (Nr - forms available for direct uptake and utilization by higher plants, including ammonia and nitrate) introduced into the environment (Vitousek et al. 1997). Galloway et al. (2004) estimated that in the 1990s anthropogenic sources of Nr accounted for ~40% of Nr production globally, a significant increase from ~6% in 1860. Fertilizer makes up 90% of the United States' industrial ammonia production, which is primarily used in the agriculture sector (Galloway et al. 2004; Kramer 2007; Galloway et al. 2007).

The use of a cover crop may also affect ecosystem OR through manipulation of N availability. Some cover crops, that are N-fixers, are used as an addition N source for crops (e.g. soybean; Snapp et al. 2005). Other cover crops are used for N immobilization, storing excess soil N in their biomass (McSwiney et al. 2010; Snapp et al. 2005). These cover crops are killed and turned into the soil prior to planting to act as a slow N fertilizer.

Agriculture May Drive OR Shifts

Shifting landscapes likely impact ecosystem OR. Land cover in the U.S. has changed significantly since the 1850s. From 1850 to 1920 forested land area decreased by ~21% due to conversion to cropland (Ramankutty and Foley 1999a). However, from 1920 to the early 1990s forest area increased by 10% due to cropland abandonment (Ramankutty and Foley 1999a). This is consistent with USDA data that show that the total aerial extent of agriculture in the U.S. has decreased by 13% from 1930 to 2010 (NASS 2010).

Agricultural ecosystems currently comprise ~34% of the terrestrial biosphere (Leff et al. 2004) and are the largest users of N fertilizer. The top five major world crops are wheat, corn, rice, barley, and soybean and they account for 22%, 13%, 11%, 9%, and 5% of cultivated land area, respectively (Leff et al. 2004). Since the 1960s, corn, soybean, and wheat have accounted for the most acreage in cropland in the United States, but prior to this corn, wheat and oats were the top 3 crops (NASS 2010; USDA 2006).

In addition, corn acreage is projected to increase over the next few years due to increases in exports and bioenergy production (USDA 2006). The latest USDA agricultural projections predict corn acreage to plateau between 35.6-36.4 million hectares after 2012 (USDA 2010). N fertilization is critical for corn ecosystem productivity and virtually every U.S. hectare of corn is treated with N (ARMS 2005). For this reason we choose a corn agricultural ecosystem to examine how N supply affects ecosystem OR.

Assumption 2: OR_{ab} is equal to OR_{ba}.

This assumption simplifies calculations of the size of the terrestrial biosphere C sink (Table 1; Randerson et al. 2006). The change in atmospheric O_2 ($\frac{dO_2}{dt}_{Atmo}$), is the sum of the amount of O_2 consumed (fossil fuels - $\frac{dO_2}{dt}_{FF}$), or released (from the terrestrial biosphere $\frac{dO_2}{dt}_{TB}$ and ocean $\frac{dO_2}{dt}_{Oc}$) over the same time period (Eqn. 4). If $OR_{ab} = OR_{ba}$, then $\frac{dCO_2}{dt}_{TB}$ can be represented simply (Eqn. 5).

$$\frac{dO_2}{dt}_{Atmo} = \frac{dO_2}{dt}_{FF} + \frac{dO_2}{dt}_{TB} + \frac{dO_2}{dt}_{Oc}$$
$$= \left(-OR_{FF} \cdot \frac{dCO_2}{dt}_{FF}\right) + \left(-OR_{net} \cdot \frac{dCO_2}{dt}_{TB}\right) + \frac{dO_2}{dt}_{Oc} \quad \text{Eqn. 4}$$

$$\frac{dCO_2}{dt}_{TB} = \left[\frac{-1}{OR_{net}}\right] \cdot \left[\frac{dO_2}{dt}_{Atmo} + OR_{FF} \cdot \frac{dCO_2}{dt}_{FF} - \frac{dO_2}{dt}_{Oc}\right] \quad \text{Eqn. 5}$$

However, it is important to evaluate this assumption carefully, because small net global offsets between OR_{ab} and OR_{ba} can cause large errors in the apportionment of anthropogenic CO_2 between the biosphere and ocean (Table 2; Randerson et al. 2006). If $OR_{ab} \neq OR_{ba}$ (Eqn. 6), then the accurate representation of $\frac{dCO_2}{dt}_{TB}$ requires a disequilibrium term (Eqn. 7).

$$\frac{dO_2}{dt}_{Atmo} = \frac{dO_2}{dt}_{FF} + \frac{dO_2}{dt}_{TB} + \frac{dO_2}{dt}_{Oc}$$
$$= \left[OR_{FF} \cdot \frac{dCO_2}{dt}_{FF}\right] + \left[OR_{ab} \cdot \frac{dCO_2}{dt}_{TB} + (OR_{ab} - OR_{ba}) \cdot \frac{dCO_2}{dt}_{ba}\right] + \frac{dO_2}{dt}_{Oc} \quad \text{Eqn. 6}$$

$$\frac{dCO_2}{dt}_{TB} = \left[\frac{1}{(OR_{ab})}\right] \cdot \left[\frac{dO_2}{dt}_{Atmo} - OR_{FF} \cdot \frac{dCO_2}{dt}_{FF} - \frac{dO_2}{dt}_{Oc} - (OR_{ab} - OR_{ba}) \cdot \frac{dCO_2}{dt}_{ba}\right] \quad \text{Eqn. 7}$$

This is because OR_{net} is the angle of a vector sum of two large gross fluxes: the flux of C from the atmosphere to the biosphere and the flux from the biosphere to the atmosphere ($\frac{dCO_2}{dt}_{ab}$ and $\frac{dCO_2}{dt}_{ba}$, respectively). CO_2 apportionment calculations use OR_{TB} (the slope of the terrestrial biosphere flux vector; Fig. 10). The terrestrial biosphere net flux vector, $\frac{dCO_2}{dt}_{TB}$, is the vector sum of the flux due to photosynthesis (from the atmosphere to the biosphere-$\frac{dCO_2}{dt}_{ab}$) and the flux due to respiration/decomposition (from the biosphere to the atmosphere-$\frac{dCO_2}{dt}_{ba}$; Fig. 10). If the slope of $\frac{dCO_2}{dt}_{ab}$ and $\frac{dCO_2}{dt}_{ba}$ (OR_{ab} and OR_{ba}, respectively) are the same (OR_{ab}=OR_{ba}) then these vectors overlap and there is no disequilibrium term (Fig. 10a, Fig. 11a; Randerson et al. 2006). A small net global difference between OR_{ab} and OR_{ba} can cause large changes in O_2 and CO_2 flux calculations (Fig.10b; Fig. 11b). Randerson et al. (2006) showed that a difference of 0.0175 between OR_{ab} and OR_{ba} is equal to a 1 Pg C yr^{-1} error in C apportionment. One Pg C yr^{-1} is 16% of global CO_2 emissions and 71% of the terrestrial biosphere's C uptake in the 1990s (Prentice et al. 2001).

Table 2. How a Disequilibrium Changes Apportionment Calculations

If $OR_{ab} \neq OR_{ba}$, then equations to calculate the rate of uptake or release of CO_2 and O_2 in the terrestrial biosphere, respectively, change. Calculating the terrestrial biosphere CO_2 uptake changes from Eqn. 5 (see Table 1) to Eqn. 7 and the OR values for photosynthesis and respiration/decomposition and the magnitude of the respiration/decomposition flux need to be known. All other equations remain the same. (Randerson et al. 2006)

Term	Formula	Value
$\frac{dO_2}{dt}_{TB}$	$= OR_{ab} \cdot \frac{dCO_2}{dt}_{TB} + (OR_{ab} - OR_{ba}) \cdot \frac{dCO_2}{dt}_{ba}$	N/A
$\frac{dCO_2}{dt}_{TB}$	$= \frac{\frac{dO_2}{dt}_{Atmo} - OR_{FF} \cdot \frac{dCO_2}{dt}_{FF} - \frac{dO_2}{dt}_{Oc} - (OR_{ab} - OR_{ba}) \cdot \frac{dCO_2}{dt}_{ba}}{OR_{ab}}$	Unk.
OR_{net}	$= \frac{\text{moles of } O_2}{\text{mole of } CO_2}$ in net terrestrial biosphere flux	1.10
OR_{ab}	$= \frac{\text{moles of } O_2 \text{ released}}{\text{mole of } CO_2 \text{ consumed}}$ in photosynthesis	
OR_{ba}	$= \frac{\text{moles of } O_2 \text{ consumed}}{\text{mole of } CO_2 \text{ released}}$ in respiration, decomposition, etc.	

Assuming that OR_{ab} and OR_{ba} are equal is equivalent to assuming that all C pools in an ecosystem are in steady state over all timescales. In other words, this assumes that decomposition, fire, and other ecosystem organic matter (OM) loss processes are releasing OM of exactly the same OR as photosynthesis has fixed in that ecosystem over a timescale of hundreds of years. Significant changes in global land use over the last 150 years render this assumption unlikely. In this paper, we compare the OR of corn ecosystem photosynthesis (OR_{ab}) to the OR of corn ecosystem respiration (OR_{ba}) over two timescales: one fallow season (the time between harvest and planting), using litterbags, and ~100 years, using soil organic matter (SOM) samples.

New Methods for Measuring Ecosystem-Level Oxidative Ratio

Directly measuring atmospheric O_2 and CO_2 concentrations from gas exchange studies can be difficult (Seibt et al. 2004; Ciais et al. 2007; Manning and Keeling 2006). Additionally, it can be hard to be confident that gas measurements reflect only ecosystem gas fluxes, with no impact from nearby fossil fuel combustion. Alternatively, we can estimate ecosystem OR from the related parameter carbon oxidation state (C_{ox}), which can be directly measured from biomass (Masiello et al. 2008). C_{ox} is a basic property of all OM, describing the average bonding environment of the C atoms in a sample. We have developed three techniques to estimate OR from plant biomass: 1) from plant carbon, hydrogen, nitrogen and oxygen (CHNO) measured using elemental analysis (Masiello et al. 2008), 2) from plant heat of combustion and %C measured using bomb calorimetry and combustion elemental analysis (Masiello et al. 2008), and 3) from solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR), plant C:N ratios, and a molecular mixing model (MMM) developed by Baldock et al. (2004) (Hockaday et al.

2009). For this paper we use both the elemental analysis and ^{13}C NMR OR techniques, which have been compared and shown to agree within ±0.005 OR units for biomass (Hockaday et al. 2009).

Here we report the OR_{ab} of the top three U.S. agricultural crops (corn, soy, and wheat grown in rotation in Michigan, USA). Additionally, we report the effects of N fertilization on corn ecosystem OR through a seven-level N fertilization rate experiment (0 to 202 kg N ha^{-1}). Finally, we examine the possibility of a disequilibrium between corn ecosystem OR_{ab} and OR_{ba} using two approaches: first, we consider short-term OR_{ab} and OR_{ba} disequilibria by comparing data for litter decomposition occurring in a conventional corn agricultural ecosystem between harvest and planting the following season; second, we consider long-term OR_{ab} and OR_{ba} disequilibria by comparing biomass OR_{ab} to OR values of the ecosystem's soil C pool.

Site Description

All samples described here were collected from the NSF-funded Kellogg Biological Station-Long Term Ecological Research station (KBS-LTER) in southwest Michigan (42°24'N, 85°24'W). For the years sampled (2003-2006), KBS received 90.8 cm, 95.9 cm, 70.2 cm, 115.6 cm of precipitation and had mean annual temperatures (MAT) of 8.6°C, 9.1°C, 9.6°C, 10.0 °C, respectively (KBS-LTER 2009). KBS soils are classified as fine-loamy and coarse-loamy mixed, mesic Typic Hapludalfs (Crum and Collins 1995). We report OR_{ab} data from the KBS-LTER Treatment 1, which consists of a corn-soybean-wheat crop rotation that undergoes conventional tillage using a chisel plow, and a typical N fertilizer application rate for this region (124 kg N ha^{-1}) (Grandy et al. 2006; Grandy and Robertson 2007). From 2003 to 2005 the crop rotation was, in order, soybean NK S20-F8 (*Glycine max L.*), soft red winter wheat Pioneer 25R37 (*Triticum aestivum L.*), and corn Pioneer 35Y54 (*Zea mays L.*). See the KBS-LTER website for more information on sampling and agronomic protocols (http://lter.kbs.msu.edu/).

We also report data from a N rate experiment performed at the KBS-LTER site. Within the N rate experiment, corn plants were fertilized with ammonium nitrate at seven N fertilization rates (0, 34, 67, 101, 134, 168, and 202 kg N ha^{-1}), applied by hand to four replicate blocks (Fig. 12). 101 kg N ha^{-1} represents N sufficient conditions for this area (McSwiney and Robertson 2005; McSwiney et al. 2010). All replicates were divided into winter wheat cover crop and no cover crop treatments (Fig. 12; McSwiney et al. 2010). In this experiment, the term *cover crop* refers to a catch crop used to prevent soil erosion and nutrient leaching during winter months and to maintain SOM. Before the corn was planted in the spring, herbicide was applied to all treatments, killing the winter wheat cover crop (while it was in a vegetative stage) before it was tilled into the soil. We present data on corn crops grown both with and without a winter wheat cover crop for all fertilization rates for replicate 1 and for all four replicates at fertilization rates 0, 67, 134, and 202 kg N ha^{-1} (to analyze natural variability). After the harvest, the corn plant was split into three plant organ types: 1) grain, 2) reproductive support (husk, shank, tassel, and cob) and 3) leaf & stem. Further details on the N rate experiment can be found in McSwiney et al. (2010).

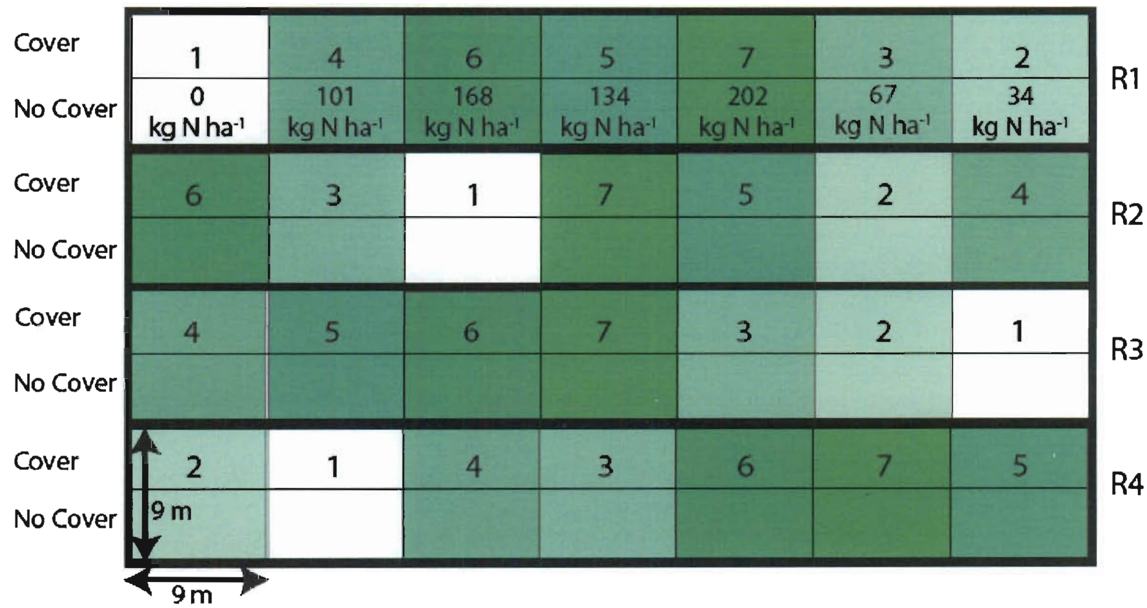

Figure 12. Nitrogen Rate Experiment

The N fertilization experiment consists of seven N fertilization treatments replicated in four and split into a winter wheat (cover) and no winter wheat cover crop (no cover). Here we present results from replicate 1 for both no cover crop and cover crop treatments over the seven fertilization rates (0, 34, 67, 101, 134, 168 and 202 kg N ha^{-1}) and replicates 2, 3, and 4 for four of the seven fertilization rates (0, 67, 134, 202 kg N ha^{-1}).

Additionally, we performed a litterbag experiment in the Treatment 1, Replicate 1 corn crop in 2005 (Fig. 13). The experiment lasted ~7 months, beginning immediately following harvest (Oct. 2005) and lasting until the next season's planting (May 2006). Litterbags were not retrieved during the winter since snow cover and cold temperatures impeded retrieval and slowed decomposition rates. Though the litterbags were not collected at random (Fig. 13), the spatial scale of the experiment is so small, it is unlikely there is a bias in the results due to a spatial trend. We also subsampled the KBS-LTER soils archive, collecting soil samples from Treatment 1 in 2005 (a corn year). Detailed information about experiments and treatments can be found at http://lter.kbs.msu.edu.

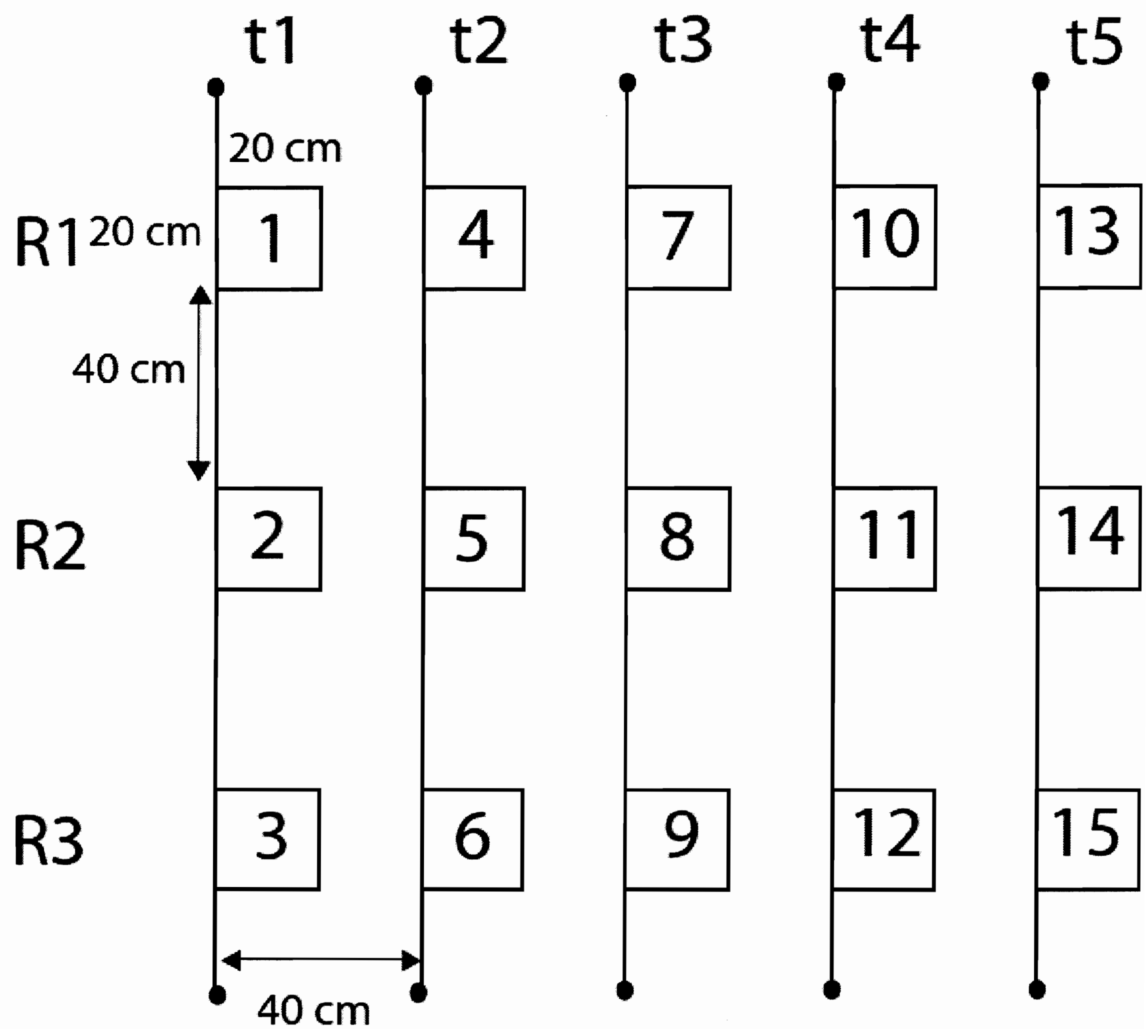

Figure 13. Litterbag Decomposition Experiment

The experimental design for the litterbag decomposition experiment in a conventional corn ecosystem (KBS-LTER T1R1). The corn crop was harvested in May 2005. Corn stover was collected and put into 15 litterbags; 3 bags were retrieved at 5 different times (t1=16 d, t2=31 d, t3=44 d, t4=182 d, and t5=206 d after deployment).

Methods

There are three ways to measure the OR of a biomass sample: 1) elemental analysis (EA) alone (requiring high precision %C, %H, %N, and %O data); 2) calorimetry coupled to %C and %N measurements (Masiello et al. 2008); and 3) ^{13}C NMR coupled to %C and %N measurements and a molecular mixing model (MMM) (Baldock et al. 2004; Hockaday et al. 2009). All of these techniques directly measure C_{ox} and then convert this value to OR. Data presented here use either the elemental analysis or the NMR technique, which agree to ±0.005 OR units (Hockaday et al. 2009). Soil OR estimates using the ^{13}C NMR cross polarization (CP) technique, are accurate to ±0.017 OR units (Hockaday et al. 2009). Error associated with soil OR measurements are higher than for biomass OR measurements because the HF (hydrofluoric acid) pretreatment of soils before analysis introduces an additional source of error.

For the KBS Treatment 1 and N rate samples we estimated OR using ^{13}C NMR because additional information on plant biochemical composition can be ascertained from the MMM in addition to C_{ox} and OR values (e.g. - Gallagher et al. In Review). The elemental analysis technique was used for litterbag data analysis, while all other samples were analyzed using the CP ^{13}C NMR technique (Table 3).

Table 3. Samples and Measurement Techniques

Sample types measured in this paper, the techniques used, and the associated error. Error for each of the T1 crops is calculated as the standard deviation of OR values from three replicated plots (Table 5). The error for the corn N Rate Experiment is based on the standard deviation of four replicated plots (Table 6). The error for the t0 litterbag experiment is the average reproducibility of the EA-derived technique reported in Masiello et al. (2008), and the error for the t1-t5 is the standard deviation of all litterbags. The error for the T1 soil OR value is the average CP ^{13}C NMR soil error as reported in Hockaday et al. (2009).

Samples	**Method**	**Error**
KBS 2003 T1 Soybean	CP ^{13}C NMR	±0.003
KBS 2004 T1 Wheat	CP ^{13}C NMR	±0.001
KBS 2005 T1 Corn	CP ^{13}C NMR	±0.002
KBS 2005 Corn N Rate Study	CP ^{13}C NMR	< ±0.006
KBS 2005 T1 Corn Litterbag Experiment (t0)	EA	±0.011
KBS 2005 T1 Corn Litterbag Experiment (t1-t5)	EA	±0.053
KBS 2005 T1 Soil	CP ^{13}C NMR	±0.017

Biomass OR analyses: ^{13}C NMR

For analysis of the Treatment 1 corn-soy-wheat biomass samples (Appendix A1) and N rate experiment samples (Appendix A3), we measured C and N concentrations using Costech 4010 and Perkin-Elmer 2400 Series CHNS/O elemental analyzers. Solid-state ^{13}C NMR was performed on a Bruker 200 MHz NMR located at Rice University. We performed cross polarization (CP) experiments (Appendices D1 and D2) using a 4mm magic angle spinning (MAS) probe, 5 kHz or 7kHz magic angle spinning (MAS) frequency, 1 ms contact time and a recycle delay >2 sec on one replicate of each plant organ under all fertilization rates. For fertilization rates 0, 67, 134, and 202 kg N ha^{-1}, CP experiments were performed on all four replicates to analyze high precision natural variability in plant biochemical composition as reported in (Gallagher et al. In Review). All spectra were corrected for spinning side bands (SSB) and spin-counted (Smernik and Oades 2001), with an average of 77.7±6.8% C detected for the N rate biomass samples. A MMM was used to estimate plant organ C_{ox} using the ^{13}C NMR spectra and the measured C and N content (Baldock et al. 2004). The MMM deconvolves a NMR spectrum into the sum of spectra of major plant biochemicals (lipid, lignin, protein, carbohydrate; Appendices B1 and B2). Whole plant C_{ox} is calculated as the weighted sum of individual biochemical C_{ox} values. For detailed information on calculating OR from NMR spectra see Hockaday et al. (2009).

2.2.2 Litterbag Estimates of OR_{ba}: Elemental Analysis

After the crop harvest of the Treatment 1, Replicate 1 conventional corn agriculture ecosystem in 2005, we performed a litterbag decomposition experiment designed to simulate conditions the crop residue (leaves and stems and reproduction support) were exposed to after harvest (Fig. 13). Approximately 13 g of corn stover and leaves were put into 15 litterbags (20 cm x 20 cm) made of fiberglass mesh and nylon thread. Leftover corn stover and leaves were saved to serve as the OR_{ab} for the ecosystem (i.e. t0 = 0 d; measured using the elemental analysis technique). Litterbags were placed back in the site where the stover was originally collected. Three litterbags were retrieved at 5 different times in a time series between October 2005 and May 2006 (t_1 = 16 d, t_2 = 31 d, t_3 = 44 d, t_4 = 182 d, t_5 = 202 d). Bags were not collected during the winter months since decomposition is slowed due to the cold temperatures. After collection, litterbags were massed, oven-dried at 60°C, massed, and compared to pre-deployment masses to determine the mass lost due to decomposition. The contents of the control biomass and each bag were ground and analyzed for CHN at the University of California – Santa Barbara Marine Sciences Institute Analytical Lab and oxygen (O) at Rice University on a Costech 4010 CHNS/O Elemental Combustion System (Appendix A2). For all litterbag samples (t_0 through t_5), CHNO elemental concentrations were used to calculate the OR of remaining biomass (Masiello et al. 2008).

Soil OR Measurements: ^{13}C NMR

We also analyzed soil samples collected from Treatment 1 in 2005 by ^{13}C NMR to estimate the entire soil pool OR value for the conventional corn soil (Hockaday et al. 2009). Soils were treated with 2% HF to demineralize samples, and a CP spectrum was acquired at 5 kHz MAS frequency, with a 1 ms contact time and ≥ 2 s recycle delay (Hockaday et al. 2009).

Calculations

OR for all samples was calculated from sample C_{ox}, and sample molar percent nitrogen and carbon, using Eqn. 8.

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3N}{4C} \qquad \text{Eqn. 8}$$

For whole crop species OR_{ab}, crop grain and residue OR values were weighted with their Net Primary Production (NPP; g m^{-2}) data (Eqn. 9; Table 4).

$$OR_{ab\ Crop} = \frac{OR_{ab\ (Grain)} \cdot NPP_{Grain} + OR_{ab\ (Stover)} \cdot NPP_{Stover}}{NPP_{Grain} + NPP_{Stover}} \qquad \text{Eqn. 9}$$

The crop OR_{ab} values for corn, soy, and wheat were weighted with total planted acreage values to estimate the U.S. Agricultural OR_{ab} value (Eqn. 10; Table 5).

$$OR_{ab\ U.S.\ Ag.} = \frac{OR_{ab\ (Corn)} \cdot \text{Planted Acres}_{Corn} + OR_{ab\ (Wheat)} \cdot \text{Planted Acres}_{Wheat} + OR_{ab\ (Soybean)} \cdot \text{Planted Acres}_{Soybean}}{\text{Planted Acres}_{Corn} + \text{Planted Acres}_{Wheat} + \text{Planted Acres}_{Soybean}} \qquad \text{Eqn. 10}$$

For the litterbag experiment, we calculated the OR_{ba} (OR for the biomass that was decomposed) at each time point by mass balance (Eqn. 11).

$$OR_{ba} = \frac{OR_{Initial} \cdot M_{Initial} - OR_{Remaining} \cdot M_{Remaining}}{M_{Lost}} \qquad \text{Eqn. 11}$$

Statistical Analyses

Statistical significance was determined using a two-tailed t-test (paired, two-sampled, unequal variance). A significance level, α, of 0.05 was used for all comparisons, indicating that p-values below this level were significant (i.e. p-values $\leq$ 0.05 imply that there is $\leq$ 5% chance of erroneously reporting differences between experimental treatments, a Type I error). T-tests were used to compare OR values between crops (soybean, wheat, and corn; Appendix C1), crop organs (grain and stover for soybean, wheat, and corn; Appendix C1), time intervals in the litterbag decomposition experiment (16 d, 31 d, 44 d, 182 d, and 206 d; Appendix C2), N fertilization rates (7 rates from 0 to 202 kg N ha^{-1}; Appendix C3), and cover crop (with and without a winter wheat cover crop; Appendix C3).

A one-way analysis of variance (ANOVA) was used to analyze the effect of time on litterbag OR_{ba} (Appendix C2). A two-way ANOVA was performed to see the effect of crop type and crop organ on OR_{ab} (Appendix C1). An analysis of covariance was also performed to determine the effects of fertilization rate, cover crop, and organ on OR_{ab} for the N Rate Experiment (Appendix C3).

Results

Agricultural OR_{ab}

We analyzed the OR_{ab} for the top three U.S. crop species, as well as the effect of agricultural management (i.e. N fertilization and cover crop) techniques on crop OR_{ab}. We also estimated the annual U.S. agricultural OR_{ab} since 1930 to test the assumption that OR is constant.

OR_{ab} for Top Three Crop Species

Whole-biomass OR for the grain and stover in the top three crops was measured (soybean, wheat, and corn in 2003, 2004, and 2005, respectively – Table 4; Fig. 14). These values represented the OR_{ab} of the ecosystem integrated over one growing season. Wheat grain and stover as well as corn stover all had OR values of 1.035 (wheat error was ±0.002, and corn error was ±0.003; both errors were calculated as the standard deviation of the average ecosystem OR values from three replicated field sites – Table 4). Corn grain had the lowest OR (1.026 ± 0.001) of all other crop tissues (Fig. 14). Soybean grain and stover had the highest OR values, at 1.143 ± 0.006 and 1.097 ± 0.002, respectively, and were both different from each other as well as wheat and corn (Table 4; Fig. 14).

Wheat stover OR values for a previous harvest year, 2001 (1.036 ± 0.001; n=2), are consistent with the 2004 wheat stover (1.035 ± 0.002; n=3). These years were comparable in MAT (2001 – 9.7 °C; 2004 – 9.1 °C) and precipitation (2001 – 1032 mm; 2004 – 959 mm). A study on the impact of precipitation and temperature on coniferous and deciduous forest leaf litter showed that though MAT varied from 7.7 °C – 10.6°C (27% variation) and total annual precipitation varied from 608 mm – 1156 mm (47%

variation), there was little variation in leaf litter OR and no correlation to precipitation or temperature (Masiello et al. 2009). It is unlikely that variations in climate year-to-year will cause shifts in crop OR, but further analysis is needed.

Combining these data with KBS-LTER net primary production (NPP) data (g m^{-2}), we calculated a crop OR (aboveground biomass only; Table 4, Table 5). OR_{ab} for soybean, wheat, and corn were 1.112 ± 0.003, 1.035 ± 0.001, and 1.030 ± 0.002, respectively and were all different from each other (p-values < 0.02; Fig. 15). A 2x3 factorial ANOVA showed that crop type, organ, and the interaction between the two are significant factors influencing OR (p-value < 0.0001). A Tukey's studentized range test was also used to compare the means and had the same results as the individual t-tests.

Table 4. OR_{ab} for Top U.S. Crops

OR_{ab} estimated from CP ^{13}C NMR experiments and the MMM developed by Baldock et al. (2004) (Hockaday et al. 2009). NPP data are available on the KBS-LTER website (http://lter.kbs.msu.edu/datatables). When available, NPP data were taken from the Annual Crop Biomass Database, specifically for 2003 whole soybean, 2004 wheat grain, 2005 grain and whole corn (KBS-LTER 2010a). Missing grain yield data were acquired from the Agronomic Yield Database (KBS-LTER 2010b). In 2004, only wheat grain yields were collected, so to calculate stover yield we used a grain:stover ratio based on the ratios for the wheat crops in 2001 and 2007 (0.403:0.597 and 0.400:0.600, respectively). Wheat grain OR is statistically the same as wheat stover OR and corn stover (t-test; p-values of 0.924 and 0.850, respectively). Wheat and corn stover OR are also the same (p-value=0.771). Corn grain and stover OR are different from each other with a p-value of 0.015. All other comparisons between crop organs are statistically significant with OR values ≤0.005 (α=0.05).

Year	Treatment	Replicate	Crop	Fraction	OR_{ab}	NPP ($g\ m^{-2}$)
2003 Soybean Grain						
2003	1	1	Soybean	Grain	1.148	129.0
2003	1	2	Soybean	Grain	1.137	179.2
2003	1	3	Soybean	Grain	1.145	175.9
2003 Soybean Stover						
2003	1	1	Soybean	Stover	1.095	364.3
2003	1	2	Soybean	Stover	1.098	323.3
2003	1	3	Soybean	Stover	1.099	359.4
2004 Wheat Grain						
2004	1	1	Wheat	Grain	1.034	319.1
2004	1	2	Wheat	Grain	1.034	350.1
2004	1	3	Wheat	Grain	1.038	401.9
2004 Wheat Stover						
2004	1	1	Wheat	Stover	1.034	478.6
2004	1	2	Wheat	Stover	1.038	525.2
2004	1	3	Wheat	Stover	1.035	602.9
2005 Corn Grain						
2005	1	1	Corn	Grain	1.027	797.9
2005	1	2	Corn	Grain	1.027	793.7
2005	1	3	Corn	Grain	1.025	914.0
2005 Corn Stover						
2005	1	1	Corn	Stover	1.035	692.7
2005	1	2	Corn	Stover	1.038	767.7
2005	1	3	Corn	Stover	1.032	960.1

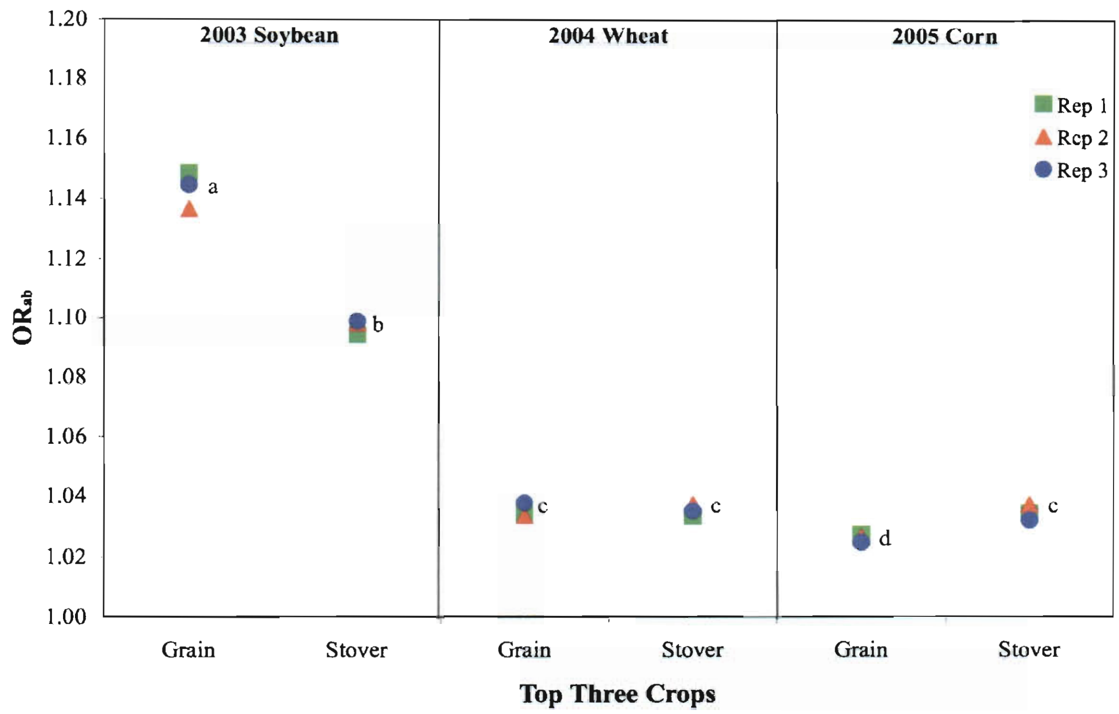

Figure 14. Agriculture OR_{ab}

OR_{ab} values for three different crops (2003 soybean, 2004 wheat, and 2005 corn) replicated in three. Each crop was split into grain and stover fractions. Letters indicate crop organs that are statistically different from each other (t-test; α=0.05).

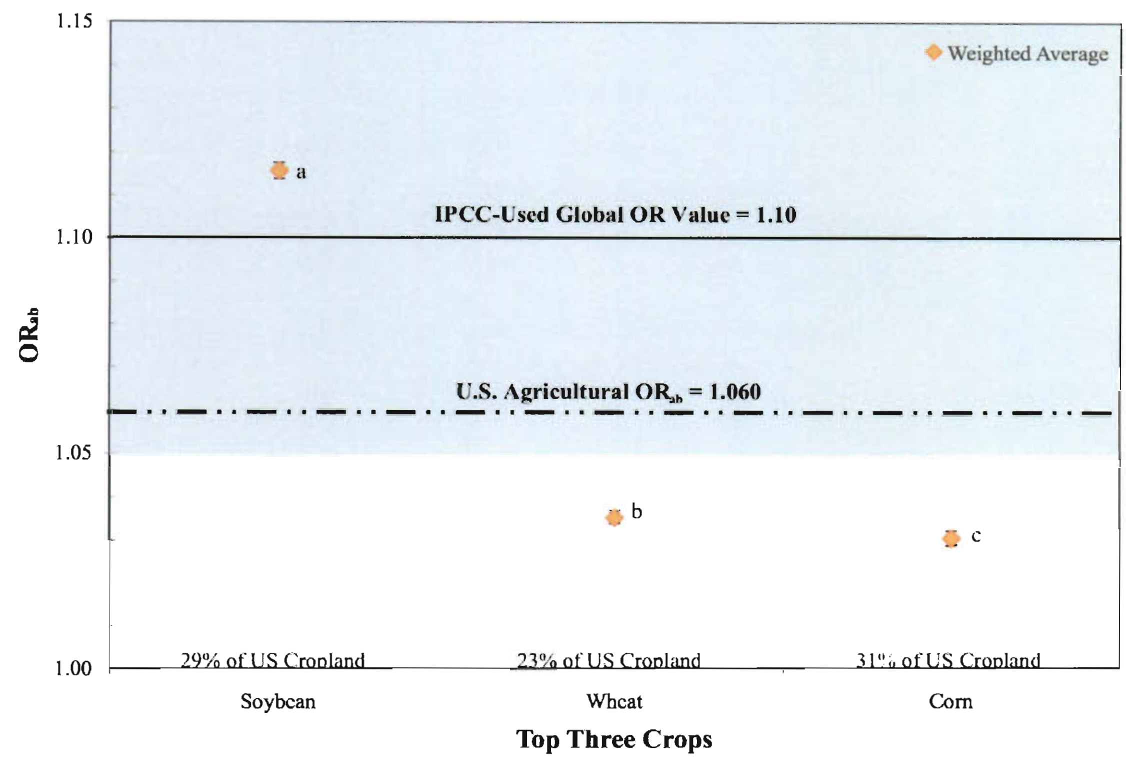

Figure 15. Crop OR and the U.S. Agricultural OR_{ab} Value

Aboveground crop (weighted average) OR_{ab} values for the top 3 crops in the United States. Crop OR_{ab} is a weighted average of grain and stover OR with NPP data. U.S. agricultural OR_{ab} is a weighted average of crop OR_{ab} with average acreage for 2003-2005 (see Table 4; soybean-29%, wheat-23%, and corn-31% of U.S. cropland - NASS 2010). The dotted and dashed line represents the U.S. agricultural OR_{ab} value, which is different from the IPCC terrestrial biosphere OR value (solid black line). The grey area represents the error bounds of the IPCC-used Global OR value (1.10 ±0.05). Soybean is different from wheat and corn (p-values = 0.00003 and 0.00001, respectively) and corn is different from wheat (p-value = 0.0185; α=0.05).

U.S. Agricultural OR

Crops represent a third of the global biosphere and in the U.S., farms comprise 40.8% of the land area (NASS 2007b). Soybean, wheat, and corn accounted for 82% of the lands used for agriculture in the U.S. in 2005 (28%, 22%, and 32%, respectively; NASS 2010). In 2010 they accounted for 86% of the lands used for agriculture with soy, wheat, and corn making up 31%, 21%, and 35% respectively (NASS 2010). Using the crop OR_{ab} averages (Table 5) and planted area data for the U.S. we calculated a 2003-2005 U.S. agriculture average OR_{ab} value of 1.060 ± 0.003, which is lower than the IPCC-used value, though this value falls within its error bounds (Eqn. 10; Table 5; Fig. 15). USDA did not provide errors in crop planted acreage data, precluding a rigorous error propagation on our U.S. agricultural OR value. We therefore did a simple error propagation using the standard deviations provided in Table 5 to capture the temporal and spatial variability of OR for these crops. The temporal-spatial variability was 0.003 OR units.

Table 5. Average OR_{ab} Values for Top Three Crop Species and U.S. Agriculture

Average OR_{ab} values are the average of replicates 1, 2, and 3 (Table 4). Weighted OR_{ab} for each crop replicate is calculated using the formula:

$$OR_{ab\,CROP} = \frac{OR_{ab\,(Grain)} \cdot NPP_{Grain} + OR_{ab\,(Stover)} \cdot NPP_{Stover}}{NPP_{Grain} + NPP_{Stover}} \qquad \text{Eqn. 9}$$

Weighted OR_{ab} in this table is the average of the weighted OR_{ab} for each replicate. U.S. agriculture OR_{ab} is a weighted average of each crops' weighted crop OR_{ab} value and their planted area average for 2003-2005. Soybean crop OR_{ab} is statistically different from wheat (p-value=0.00003) and corn (p-value=0.00001). Wheat and corn crop OR_{ab} are also different from each other (p-value=0.018; α=0.05).

Year	Crop	Organ	Avg. OR_{ab}	Std. Dev. OR	Avg. NPP	Std. Dev. NPP	Crop OR_{ab}	Crop OR_{ab} Error	Avg. Area (1000 ha)	U.S. Agriculture OR_{ab}
2003	Soybean	Grain	1.143	0.006	161.4	28.1	1.112	0.003	29764	1.060 (± 0.003)
2003	Soybean	Stover	1.097	0.002	349.0	22.4				
2004	Wheat	Grain	1.035	0.002	357.0	41.9	1.035	0.001	24146	
2004	Wheat	Stover	1.035	0.002	535.6	62.8				
2005	Corn	Grain	1.026	0.001	835.2	68.3	1.030	0.002	32552	
2005	Corn	Stover	1.035	0.003	806.8	137.9				

U.S. Agricultural OR Over Time

Using the crop OR_{ab} averages, U.S. planted acreage data from the 1930s to present, we estimated changes in U.S. agricultural OR_{ab} over time (Fig. 16). In our calculations, we made the assumption that any temporal changes in the OR of a given crop species fell within the spatio-temporal variation measured at KBS from 2003-2005 (±0.006). Corn, wheat, and soybean have been the top 3 crops grown in the United States since 1963, accounting for 64%-87% of total planted acreage depending on the year (NASS 2010). Before 1963 corn, wheat, and oats were the top 3 crops. Since we did not measure OR for oats we estimated it using oaten hay biochemistry data (Nelson and Baldock 2005). Our OR_{ab} estimate for oats was 1.081. This OR was higher than that of corn and wheat likely because oats have the highest concentration of protein of any cereal crop (Vaughan and Geissler 2009), but is not as high as soybean since oats are not legumes. Given the assumptions made in this calculation, the U.S. agricultural OR_{ab} has increased from 1.040 in 1930 to 1.060 in 2010 (Fig. 16).

Effect of Nitrogen Fertilization on Corn Ecosystem OR_{ab}

Fertilization rate, crop organ, and interactions between the two, influence OR_{ab} (ANCOVA results: p-values < 0.0001). Fertilization did not significantly affect plant organ OR_{ab} (i.e. corn grain, reproductive support, and leaves and stems) despite altering corn biochemistry (Gallagher et al., in review). There was a significant difference between OR values for only the leaf and stem when comparing unfertilized and fertilized plants grown with higher N rates (134 and 202 kg N ha^{-1}) in the presence or absence of a cover crop (p-values range from 0.003-0.05; Table 6). MMM results suggested that this was due to increases in protein and lignin stocks (Gallagher et al. In Review).

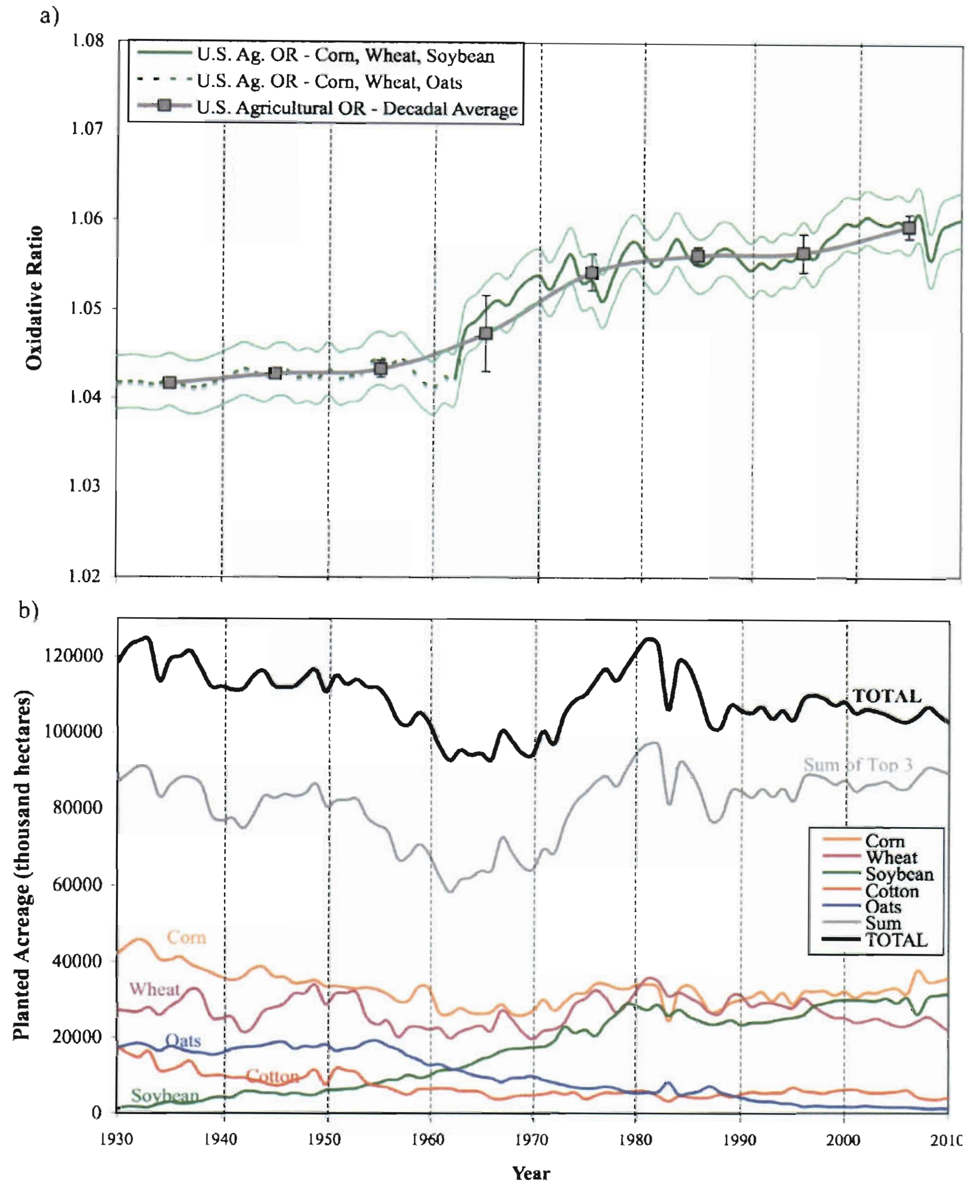

Figure 16. U.S. Agricultural OR has Shifted Over the Last 80 Years

a) U.S. agricultural OR is calculated as the weighted average of the top 3 crops' (by planted acreage) aboveground OR. From 1963 until present the top 3 crops have been corn, 1.030, wheat, 1.035, and soybean, 1.112 (see Fig. 16b). Before 1963, oats was the third most abundant crop. Since we did not measure OR for oats we estimated it as 1.081 using oaten hay biochemistry data (Nelson and Baldock 2005). The dashed line represents a U.S. agricultural OR value estimated using corn and wheat OR measured values and oat OR estimated value. Grey squares with error bars represent the decadal U.S. agricultural OR value (e.g. average OR from 1930 to 1939). Light grey lines represent the upper and lower error bounds. b) U.S. crop planted acreage (thousand hectares) for corn, soybean, wheat, cotton, oats, the sum of the top 3 crops for that year, and the total planted crop acreage for that year. The top 3 crops represents between 65%-87% of total U.S. crop planted acreage depending on the year (NASS 2010).

Biosynthesis of protein and lignin are both limited by N availability (van Rensburg et al. 2000; Erisman et al. 2007) and the carbon in protein and lignin is more reduced (has higher OR values) than the carbon in carbohydrates. Therefore increased protein and lignin contents should result in the higher OR value for leaves and stems at higher fertilization rates (Masiello et al. 2008). Observed shifts in OR were minor, especially when compared to the difference in OR between crop species or with the IPCC value (Table 6).

We detected extremely small changes in ecosystem OR for the no cover crop treatment with fertilization, with a shift from a whole plant OR of 1.036±0.001 at 0 kg N ha^{-1} to a whole plant OR of 1.039±0.002 at 202 kg N ha^{-1}. This shift of 0.3% was significant at p-value=0.05, but represents a very small change in response to almost twice recommended N application levels (Table 6 and Fig. 17). There was no statistically significant response for whole plant OR over the N gradient with the cover crop treatment (1.035±0.004 at 0 kg N ha^{-1} and 1.041±0.003 at 202 kg N ha^{-1}). The difference observed in the no cover crop treatment (1.036 vs. 1.039 at the gradient extremes) is very small compared to the difference between corn and soybean OR (0.090 units; 30 times larger) or corn and the IPCC-used global biosphere value (0.070 units). We conclude that corn ecosystem OR is remarkably constant with respect to N fertilization, varying at most in the third decimal place.

Effect of a Cover Crop on Corn Ecosystem OR_{ab}

The use of a cover crop also has no effect on total crop, crop residue, grain, reproductive support or leaf & stem OR, with p-values ranging from 0.26 to 0.95, all above the significance threshold (Fig. 17; Table 6). An analysis of covariance supports this, with cover crop having no significant impact on OR (p-value =0.3204), not even when interacting with fertilization rate (p-value=0.3075) or organ (0.9943). All 4 replicated cover/no-cover pairs were within 0.002 OR units. An average of all OR values for the total corn plant at any fertilization rate and replicate was 1.037 ± 0.003 and 1.037 ± 0.002 for corn grown with and without a cover crop, respectively (Table 6). All OR values measured at this N fertilization experiment are significantly lower than the global biosphere estimate used by the IPCC (Fig. 17).

Table 6. Corn Ecosystem OR Under Different Agricultural Management Strategies

OR_{ab} values for corn grain, reproductive support, leaf & stem, crop residue, & total plant grown under varying N fertilization rates and cover crops. Average OR_{ab} is the average of OR_{ab} for Replicates 1-4 (n=4). Error is the natural variability of OR_{ab}.

		Cover Crop			No Cover Crop		
	Fertilization Rate (kg N ha^{-1})	**Rep 1 OR_{ab}**	**Average OR_{ab}**	**Error**	**Rep 1 OR_{ab}**	**Average OR_{ab}**	**Error**
Corn Grain	0	1.028	1.028	0.004	1.030	1.029	0.002
	34	1.033			1.030		
	67	1.035	1.031	0.003	1.030	1.031	0.002
	101	1.030			1.031		
	134	1.032	1.031	0.001	1.030	1.032	0.003
	168	1.035			1.030		
	202	1.039	1.035	0.003	1.032	1.033	0.002
Reproductive Support	0	1.035	1.037	0.004	1.038	1.037	0.002
	34	1.037			1.033		
	67	1.034	1.035	0.001	1.039	1.035	0.004
	101	1.035			1.035		
	134	1.033	1.034	0.002	1.031	1.035	0.003
	168	1.038			1.040		
	202	1.036	1.036	0.002	1.036	1.035	0.002
Leaf & Stem	0	1.035	1.041	0.006	1.041	1.042	0.001
	34	1.039			1.044		
	67	1.044	1.045	0.002	1.045	1.045	0.001
	101	1.049			1.054		
	134	1.054	1.050	0.003	1.044	1.050	0.004
	168	1.051			1.045		
	202	1.057	1.051	0.004	1.050	1.051	0.003
Crop Residue	0	1.035	1.040	0.005	1.040	1.041	0.001
	34	1.039			1.042		
	67	1.042	1.043	0.002	1.044	1.043	0.001
	101	1.046			1.049		
	134	1.048	1.046	0.002	1.041	1.046	0.004
	168	1.047			1.044		
	202	1.052	1.047	0.003	1.047	1.047	0.002
Total Corn Plant	0	1.032	1.035	0.004	1.036	1.036	0.001
	34	1.036			1.036		
	67	1.038	1.036	0.002	1.036	1.036	0.001
	101	1.037			1.039		
	134	1.039	1.037	0.001	1.035	1.038	0.003
	168	1.040			1.036		
	202	1.045	1.041	0.003	1.039	1.040	0.002

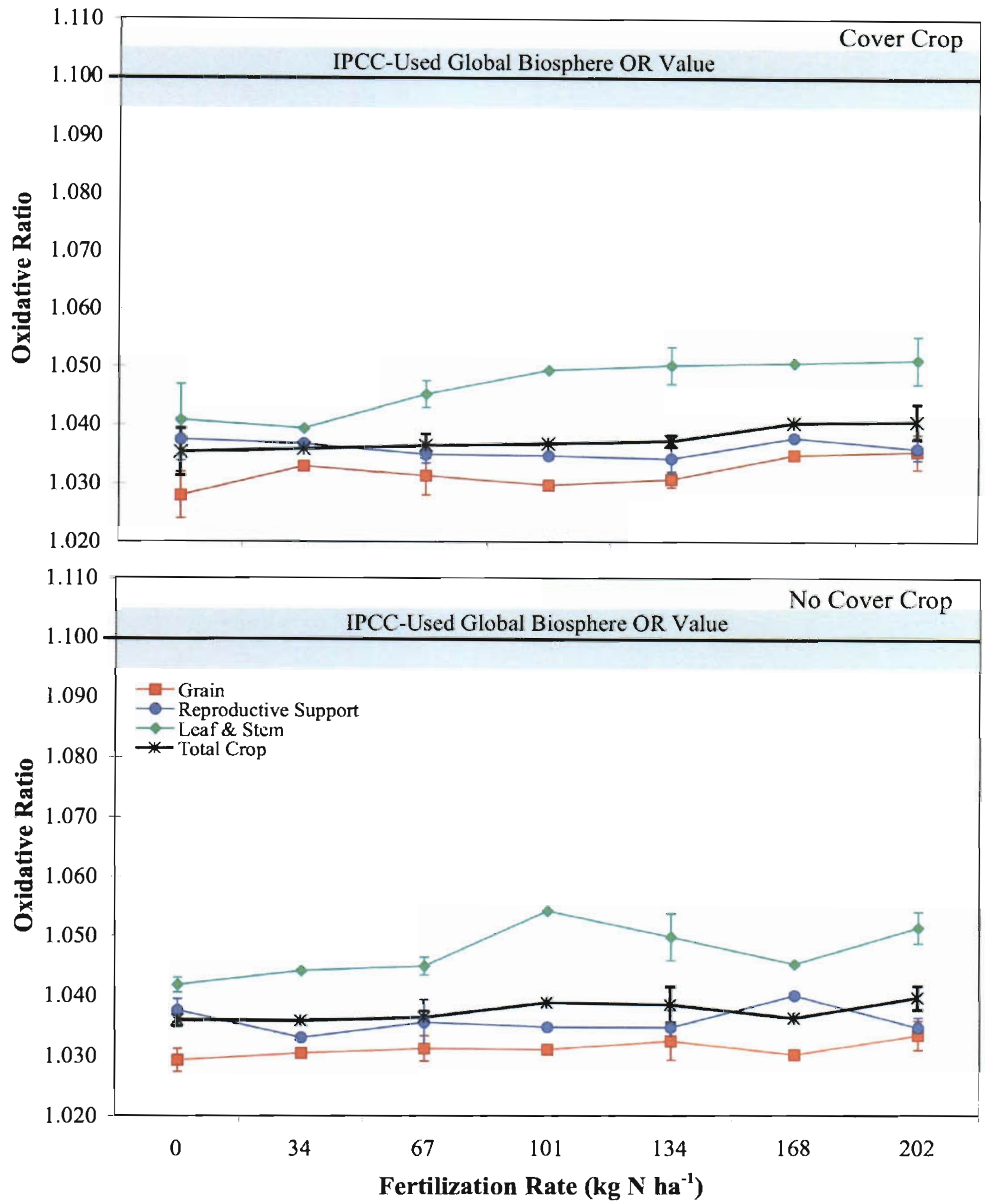

Figure 17. N Fertilizer & Cover Crop Have no Effect on Crop or Crop Organ OR

OR_{ab} values for corn grain, stover, reproductive support and total crop were measured at the N rate experiment at KBS-LTER. For fertilization rates 0, 67, 134, and 202 kg N ha^{-1} values are the average ecosystem OR between replicates 1, 2, 3, and 4, with error bars representing the natural variability of ecosystem OR and are the standard deviation for the average of four replicates (Table 6). For fertilization rates 34, 101, 168 kg N ha^{-1}, values are ecosystem OR values for replicate 1 (Table 6). The left panel represents OR values grown with a winter wheat cover crop and the right panel are OR values for corn grown without a winter wheat cover crop.

Agricultural OR_{ba}-The Decomposition Flux

The starting (t_0) OR value for the litterbag decomposition sequence, OR_{ab} in Treatment 1, Replicate 1 for the corn stover in 2005 was 1.038±0.011 (Table 7). This was measured using the elemental analysis technique and is the same as the OR estimated from the NMR technique on 2005 corn stover (Treatment 1 average = 1.035 ± 0.003; see Table 4). In our short-term litterbag experiment, OR_{ab} is the same as OR_{ba} (Table 8; Fig. 18). All OR_{ba} values for times t_1 through t_5 were the same (p-values ranging from 0.086 to 0.967), except for t_3 and t_4, which were statistically different from each other (p-value =0.012). An analysis of variance showed time to influence OR (p-value =0.0473). A Tukey's studentized range test was also performed to compare the means, showing that t1 and t5 were significantly different from each other with all other time points the same. The average OR_{ba} for all litterbags at all times was 1.028 ± 0.053. The large errors associated with the litterbag decomposition experiment are likely attributed to fauna damaging the litterbags and removing biomass (the litterbag experiment relies on the assumption of conservation of mass).

Table 7. Litterbag Oxidative Ratio

Litterbag OR of the remaining biomass is measured using the elemental analysis technique and combined with mass data (ratio of mass lost to initial mass), OR_{ba} for each litterbag is calculated using Eqn. 11. Bags 1-3, 4-6, 7-9, 10-12, and 13-15 were collected on day 16, 31, 44, 182, and 202, respectively.

OR_{ab}: 1.038

Bag	Mass Loss Ratio (g)	OR Remaining	OR Lost (OR_{ba})
1	0.1	1.034	0.970
2	0.1	1.032	1.056
3	0.1	1.034	1.023
4	0.1	1.036	1.014
5	0.1	1.028	1.086
6	0.3	1.051	0.985
7	0.1	1.042	0.996
8	0.2	1.044	0.983
9	0.1	1.043	0.941
10	0.4	0.986	1.117
11	0.3	1.010	1.119
12	0.2	1.030	1.054
13	0.3	1.052	0.992
14	0.4	1.020	1.068
15	0.2	1.047	1.019

Table 8. Corn Ecosystem OR_{ba}

Average and standard deviations for the OR of the biomass remaining and OR_{ba} at retrieval times t_1=16 d, t_2=31 d, t_3=44 d, t_4=182 d, and t_5=206 d, calculated from Table 7.

OR_{ab}: 1.038±0.011

t	Time (days)	Avg. OR Remaining	Std. Dev. OR Remaining	Avg. OR Lost (OR_{ba})	Std. Dev. OR Lost (OR_{ba})
1	16	1.034	0.001	1.016	0.043
2	31	1.038	0.011	1.028	0.052
3	44	1.043	0.001	0.973	0.029
4	182	1.009	0.022	1.097	0.037
5	206	1.039	0.017	1.027	0.038

We can compare our data to one other litterbag OR experiment performed by Baldock et al. (2004), who buried corn residue in agricultural soil for 582 d (3x as long as our experiment). Using molar ratio data from Baldock et al. (2004), we calculated the OR values of their remaining biomass (avg. 1.042 ± 0.020). Although Baldock et al (2004) measured the OR of their corn litter via ^{13}C NMR and we measured the OR of our corn litter via elemental analysis, our average remaining sample OR of 1.033 ± 0.017 is indistinguishable from theirs (Fig. 18).

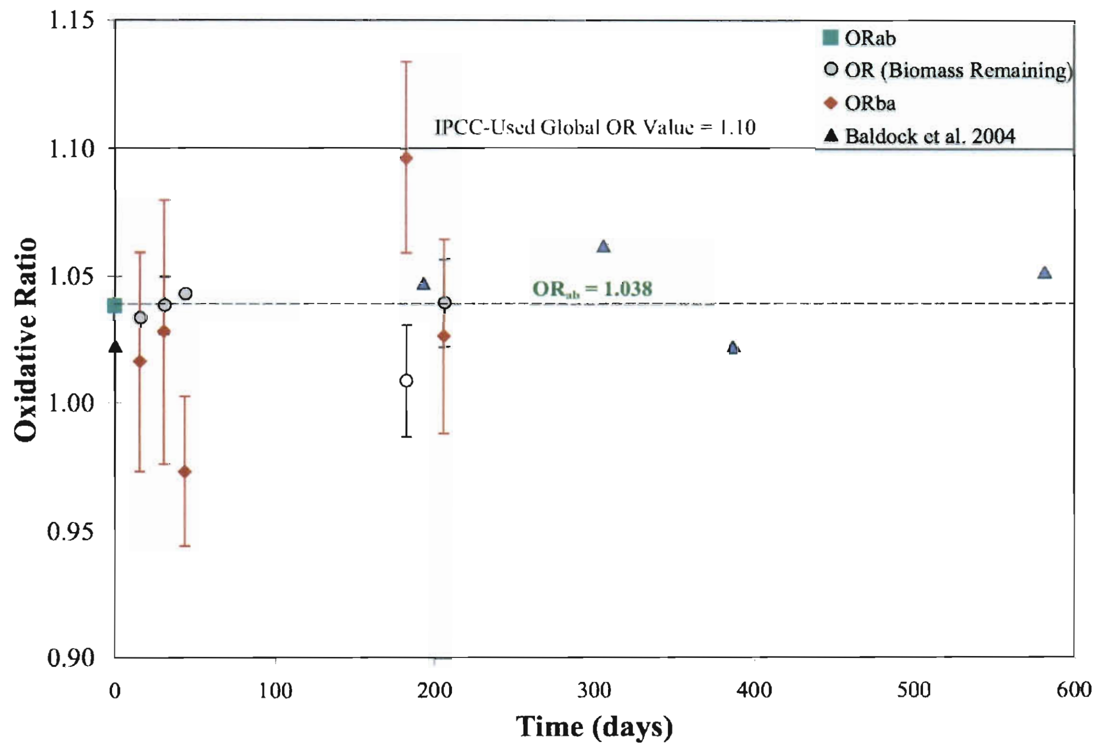

Figure 18. Corn Ecosystem OR_{ba} (Decomposition Experiment)

OR results for two litterbag decomposition experiments. The solid black square is the OR value of the biomass harvested (OR_{ab}). The grey open circle is the OR for the biomass remaining after varying amounts of decomposing time have passed (16 d, 31 d, 44 d, 182 d, and 206 d). Solid black diamonds are the OR_{ba} for each time-step calculated from OR_{ab} and the OR of the biomass remaining using Eqn. 11. Open triangles represent data from decomposition experiment over 582 d of corn residue buried in agricultural soil performed by Baldock et al. (2004).

An OR value was also measured for the soil in Treatment 1, Replicate 1 in 2005 using CP ^{13}C NMR. This is the OR of the bulk SOM pool and is not an OR value associated with a flux (i.e. photosynthesis – OR_{ab}, or decomposition/respiration – OR_{ba}). This is the OR of the OM remaining after decomposition over longer timescales (see Eqn. 11). The bulk soil OR was 1.089±0.017, significantly higher than the OR_{ab} for corn from this site (1.035±0.003). There is no detectable difference between the bulk soil OR and OR_{ba} due to the large error associated with the litterbag experiment (1.028±0.053).

Discussion

OR of Agriculture is Not Constant

Our results show that OR is neither constant over space nor time within the spatial and temporal boundaries of the KBS-LTER. OR varied within the agricultural ecosystems studied depending on crop species, and changing agricultural extent and species composition has been estimated to lead to temporal variations in agricultural OR on a national scale. However, we did observe constancy in crop OR when varying two agricultural management techniques: 1) N supply, and 2) cover crop.

<u>Crop Oxidative Ratio Varies Between Species</u>

Soybeans have a higher OR (1.112 ± 0.003), likely because they are a N-fixing species and richer in protein (Table 5). The average OR of proteins, 1.13, is higher than most other biochemicals (Masiello et al. 2008). Wheat and corn had lower OR values, averaging 1.035 ± 0.001 and 1.030 ± 0.002, respectively, which are significantly different from the IPCC-used terrestrial biosphere estimate (Table 5). These have OR values closer to 1.00 since both of these crops are primarily composed of carbohydrates (i.e. sugars, cellulose, hemicellulose; Gallagher et al. In Review).

<u>U.S. Agricultural OR Has Changed Over the Past 80 years</u>

Figure 16 shows how agriculture extent and crop composition has varied over the past 80 years leading to an increase in U.S. agricultural OR from 1.030 in the 1930s to 1.060 in 2010. The time variation in this figure demonstrates the influence of cropland composition on OR. This increasing trend was primarily driven by the increase in soybean acreage from 1963 until present (Fig. 16b). Before 1963, the small increase in agricultural OR was caused by a simultaneous decrease in corn crop acreage and an increase in soybean acreage. Ongoing shifts in U.S. cropping, driven by demand for corn ethanol, are likely to lead to a drop in OR. It is possible that genetic improvements of crops (i.e. to increase productivity, drought tolerance, disease resistance, N use efficiency, etc.) may also alter crop and agricultural OR.

OR_{ab} Versus OR_{ba}

For the 2005 corn ecosystem, no disequilibrium existed on the short-term between OR_{ab} (1.038 ± 0.003) and OR_{ba} (1.028 ± 0.053), as determined in a 202-day litterbag experiment. This is likely a function of the experimental design being limited, resulting in the large error associated with OR_{ba}. However, the bulk soil OR value was quite different: 1.089 ± 0.017 for the whole SOM pool in Treatment 1, Replicate 1 in 2005. Interpreting soil pool OR values is more challenging than interpreting biomass pool OR values. The majority of aboveground biomass decomposes within a timescale of years, making it reasonable to assume that the OR of an entire biomass pool is a good proxy for the OR of surface litter. However, SOM turnover is slower than surface litter, and cannot be characterized by a single rate law, making it difficult to estimate the OR of SOM turnover flux.

The bulk soil OR value, 1.089 ± 0.017, is different from the OR_{ab} (1.038 ± 0.003) for the corn in this agricultural ecosystem. There are three possible explanations for the 0.051 unit offset between the bulk soil OR and the OR_{ab} of the corn biomass. These explanations are: 1) soil has remnant organic matter from many previous growing seasons and perhaps native ecosystems (e.g. forest), 2) roots with higher OR are a significant source of soil C, driving an offset between soil and aboveground biomass, and 3) OR fractionation occurs during decomposition. We show below that the most plausible explanation for the biomass OR_{ab}/soil OR offset at this site is the slow fractionation of OR during decomposition, leading to a long-term offset between OR_{ab} and OR_{ba} too slight for us to detect within the error of our year-long litter bag decomposition experiment (±0.053). It should be noted that here we are comparing OR values measured with different techniques (bulk soil OR – CP ^{13}C NMR and OR_{ab} and OR_{ba} from litterbags – elemental analysis), and that these methods are comparable to within ±0.017 (Hockaday et al. 2009).

The first possible explanation for the difference between the bulk soil and the corn litter OR_{ba} values is that the soil value simply reflects the average of the biomass from a three crop rotation. The soybean residue is likely partially responsible for the OR_{ba} value being higher (soybean stover: OR = 1.097; corn & wheat stover: OR = 1.035; Table 4). However, if we assume that all three residues impact bulk soil OR equally, the bulk soil OR should be 1.055±0.003. If we weight crop OR with crop residue NPP the average is even lower, 1.048±0.003, since wheat and corn contribute more by mass. Both of these averages are significantly different from the observed value of 1.089±0.017. This cannot be the sole mechanism.

The second possible explanation is that the precursor, forest ecosystem is controlling the bulk soil OR. The KBS-LTER agricultural treatments were established in 1989; however, this site had been cultivated for at least 100 years prior to the establishment of the KBS-LTER (Robertson et al. 1997). KBS-LTER is located where natural ecosystems are hardwood forests (Kuchler 1964; Robertson et al. 1997). It is possible that remnant forest SOM (including charcoal from forest fires) contributes to the soil OR given that some soil OM fractions have ^{14}C signatures indicating C fixed before 19th century forest clearing in this area (Paul et al. 2001; 2003), and approximately 17% of the soil C is attributed to charcoal by MMM analysis of the CPMAS ^{13}C NMR data. We measured the OR of SOM in the upper 25 cm of the remnant hardwood forest. The native forest SOM has an OR value of 1.108 ±0.006, which is what we would expect the agricultural field OR_{ba} value to be if agriculture crops did not contribute significantly to SOM. Given that the value measured for the SOM (1.089±0.017) lies between that of the adjacent forest and the weighted mean value of agricultural inputs (1.048), it is possible that the measured OR value is representative of a mixture of old forest and new agricultural C. Assuming a linear mixing model where the forest and represent the extremes, the measured OR value would suggest that 68% of the SOM present was remnant from the original forests. These calculations assume that all belowground C has the same OR value as the no selective decomposition or preservation of particular forms of organic matter occurred in the soil.

A third possibility is that roots with a very high OR_{ab} value are the primary input of biomass into the SOM pool. We do not have root samples for any of the crops analyzed, so we cannot report root OR values. However, OR values calculated for roots, stems, and leaves for woody and herbaceous plants show no large differences between above- and belowground biomass (Randerson et al. 2006). For woody plants, roots are calculated to be within 0.003 OR units of leaves (1.051 for roots and 1.054 for leaves; Randerson et al. 2006). For herbaceous plants, roots are calculated to have a lower OR than leaves (1.025 versus 1.031), making it challenging to argue that root OR values could drive SOM OR values up.

The final possibility is that OR is fractionated during decomposition. As litter enters the soil pool and is decomposed by microbes, the microbes are consuming simpler compounds with lower OR values (1.00), leaving behind an "enriched" litter material, with a higher OR value than it had originally. Although there was no significant difference between OR_{ab} and OR_{ba} in the litterbag experiment, the observed, nonsignificant drop in OR (1.038±0.011 to 1.028±0.053) is consistent with the initial decomposition of simple, easily decomposed compounds (i.e. carbohydrates; OR = 1.00). Microbial decomposition changes litter chemistry (Berg 2000; Dilly et al. 2001; Fioretto et al. 2005; Papa et al. 2008), and soil invertebrates have also been shown to change the chemical composition of SOM through preferential ingestion of specific plant parts (Crow et al. 2009).

If the process of SOM decomposition fractionates OR (as we suggest above), the implication is that SOM diagenesis drives a small, long-term O_2 flux from soils that is compensated for globally through processes that completely decompose SOM (e.g. fire). The OR_{ba} of fire has been estimated at 1.091±0.003 (Hockaday et al. 2009), very close to our bulk soil OR of 1.089±0.017. If this is the case, then for this ecosystem there is no offset-driven excess O_2 flux. However, our results do not mean that such an offset does not exist globally due to land use change.

OR in a Nitrogen Cycle Context

N-cycle driven O_2 and CO_2 fluxes are large enough that they must be included in global scale CO_2 and O_2 flux calculations of ocean and biosphere C sinks (Ciais et al. 2007). Because some, but not all, N-cycle driven gas fluxes are included within OR measurements, it is important that ecosystem-scale OR measurements such as ours acknowledge explicitly whether they contain N_2-derived oxygen fluxes so that there is no double-counting in CO_2-O_2 diagrams.

The production and use of fertilizer creates a net atmospheric O_2 sink (Ciais et al. 2007). Ten percent of fertilizer is produced as NH_4NO_3, and the O_2 required to convert N_2 into nitrate results in an immediate flux of 0.7 Tmol O_2 yr^{-1} out of the atmosphere

(Ciais et al. 2007). The remaining 90% of fertilizer N is in ammonium functional groups, and the majority of this NH_4 is converted to nitrate prior to plant uptake or ecosystem loss. Nitrification of NH_4 from fertilizer creates a much larger O_2 sink of 16.4-31.6 Tmol O_2 yr^{-1} (Ciais et al. 2007), comparable in size, but opposite in direction, to the amount of O_2 degassed by warming oceans (30±40 Tmol O_2/year - Keeling and Garcia 2002). Finally, plant uptake of NO_3^- causes a flux of O_2 back to the atmosphere, releasing ~12 Tmol O_2 yr^{-1} (Ciais et al. 2007).

Additionally, there are atmospheric CO_2 sources associated with anthropogenic perturbations to the global N cycle. For example, when microbes use fertilizer-derived NO_3^- as a terminal electron acceptor, organic matter is converted to CO_2. Additional CO_2 fluxes result from waste ammonification and from changes in plant N_2 fixation caused by land use change (Ciais et al. 2007).

Our OR measurements reflect ecosystem-scale boundaries: we report OR_{ab} and OR_{ba} data for individual ecosystems within the KBS-LTER field site. This ecosystem-scale approach is typical for biospheric gas flux studies, and follows logically from any attempt to measure OR. All other studies measuring ecosystem OR have similarly drawn ecosystem-scale boundaries (e.g. Stephens et al. 2007; Seibt et al. 2004). The choice of ecosystem-scale boundaries means that our OR data include some, but not all of the O_2 and CO_2 perturbations from fertilizer production. Nitrification of NH_4 and plant uptake of nitrate are both wrapped into the OR values we report because both of these processes occur within our ecosystem. The 0.7 Tmol yr^{-1} O_2 flux from fertilizer production is not included, as fertilizer production does not occur within the boundaries of our ecosystem. CO_2 sources from denitrification and ammonification are not included, as these do not occur significantly within the boundaries of our agricultural ecosystems either. It is also the case that while some N-cycle driven O_2 fluxes are included in our OR data, these fluxes do not necessarily occur in globally representative ways within an agricultural ecosystem. For example, nitrification of NH_4^+ may occur disproportionately within fertilized ecosystems. Our OR values should not be taken as globally representative; instead, globally representative OR values should be constructed based on measurements of many types of ecosystems.

When ecosystem-scale OR measurements such as ours are used in O_2/CO_2 calculations, we recommend that the O_2 flux associated with fertilizer production be added as a unique vector. Ideally, our data should be spatially averaged with data on ecosystems where other N-cycle O_2 fluxes occur to produce a global ecosystem OR value that reflects denitrification and ammonification-drive O_2 fluxes.

Conclusions

We show that OR of agricultural ecosystems are neither constant over time or space, instead varying with crop species (Fig. 19). The OR values of corn and wheat, (1.030±0.001 and 1.035±0.003, respectively) are significantly lower than the IPCC-used estimate of global biosphere OR (1.10±0.05). The OR of soybeans is 1.112±0.003. The modeled average OR values of US agricultural ecosystems have changed over the past 75 years, rising from 1.040 in 1930 to 1.060±0.003 in 2005. This change is primarily a result of the expansion of soybean crops and assumes that the OR_{ab} values for crop species has not changed over this period. Although N application has the potential to change crop biochemistry, we show that for corn, N fertilizer causes almost negligible shifts in ecosystem OR even at twice the recommended fertilizer application rates.

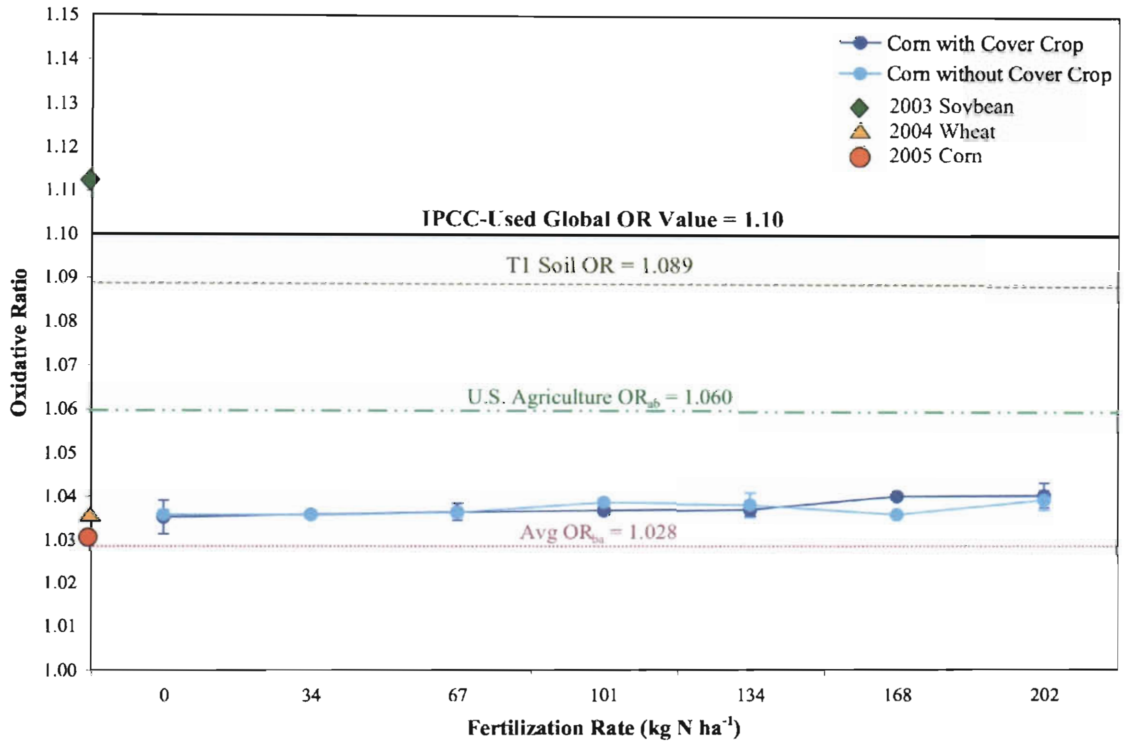

Fig. 19. Agricultural Oxidative Ratio

The solid dark grey circles represent ecosystem OR of the corn crop grown with a cover crop over a N fertilization gradient. For fertilization rates 0, 67, 134, and 202 kg N ha^{-1}, values are the average ecosystem OR between replicates 1, 2, 3, and 4, with error bars represent the natural variable of Ecosystem OR. For fertilization rates 34, 101, 168 kg N ha^{-1} values are ecosystem OR values for replicate 1. The solid light grey circles represent ecosystem OR of the corn crop grown without a cover crop over a N fertilization gradient. For fertilization rates 0, 67, 134, and 202 kg N ha^{-1} values are the average ecosystem OR between replicates 1, 2, 3, and 4, with error bars represent the natural variable of Ecosystem OR. For fertilization rates 34, 101, 168 kg N ha^{-1}, values are ecosystem OR values for replicate 1. Solid symbols on the y-axis represent crop OR_{ab} for the 2003 soybean (black diamond), 2004 wheat (black triangle), and 2005 corn (black circle). The dotted black line represents the average OR_{ba} value for the decomposition experiment $OR_{ba} = 1.028 \pm 0.053$. The dashed black line represents the OR_{ba} value for Treatment 1 soil OR = 1.089. The dot, dot, dashed black line represents our calculated U.S. agriculture OR_{ab} value $OR_{ab} = 1.060$. The solid black line is the IPCC-used value 1.10 ± 0.05.

Over an annual timescale we show no measurable offset between the OR values of photosynthesis and decomposition (OR_{ab} and OR_{ba}), due to the large error associated with the technique. However, we do find a significant offset between OR_{ab} and the bulk OR values of the SOM pool, with soil having significantly higher OR values than biomass. The most plausible explanation for this offset at our field site is likely a combination of 1) fractionation of the OM OR during the process of SOM diagenesis, with decomposition preferentially consuming OM with lower OR values (e.g. carbohydrates), and 2) domination of the bulk soil OR value by the precursor, forest ecosystem's OR value. An OR offset occurring naturally during the process of SOM decomposition does not cause a global, net offset between OR_{ab} and OR_{ba} as long as the processes of SOM formation and destruction are in equilibrium. If these processes are not in equilibrium, however, net O_2 fluxes may result, skewing OR-based anthropogenic CO_2 apportionment calculations.

CHAPTER 3

Biochemical Suitability of Crop Residues for Cellulosic Ethanol: Disincentives to Nitrogen Fertilization in Corn Agriculture

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In Review at

Environmental Science & Technology

Submitted on September 24, 2010

Abstract

Concerns about energy security and climate change have increased biofuel demand, particularly ethanol produced from cellulosic feedstocks (e.g. food crop residues). A central challenge to cropping for cellulosic ethanol is the potential environmental damage from increased fertilizer use. Previous analyses have assumed that cropping for carbohydrate in residue will require the same amount of fertilizer as cropping for grain. Using ^{13}C nuclear magnetic resonance, we show that increases in biomass in response to fertilization are not uniform across biochemical classes (carbohydrate, protein, lipid, lignin) or tissues (leaf and stem, grain, reproductive support). Although corn grain responds vigorously and non-linearly, corn residue shows only modest increases in carbohydrate yields in response to high levels of fertilization (25% increase with 202 kg N ha^{-1}). Lignin yields in the residue increased almost twice as fast as carbohydrate yields in response to nitrogen, implying that residue feedstock quality declines as more fertilizer is applied. Fertilization also increases the decomposability of corn residue, implying that soil carbon sequestration becomes less efficient with increased fertilizer. Our results suggest that even when corn is grown for grain, benefits of fertilization decline rapidly after the ecosystem's N needs are met. Heavy application of fertilizer yields minimal grain benefits and almost no benefits in residue carbohydrates, while degrading the cellulosic ethanol feedstock quality and soil carbon sequestration capacity.

Introduction

Rising oil prices and growing concerns over greenhouse gas emissions and climate change have increased demand for biofuels, particularly for corn grain ethanol (Solomon et al. 2007; Hill et al. 2006; Service 2007). Increasing demand for corn grain ethanol is increasing corn acreage (8% increase in acreage in the U.S. from 2004-2009; NASS 2010) leading to: decreased crop diversity (Landis et al. 2007), increased soil erosion, and increased use of nitrogen (N) fertilizers, pesticides, and herbicides (Pimentel et al. 2009; McLaughlin and Walsh 1998; Patzek 2004). However, ~1.02 billion people are undernourished (FAO 2009), making the use of corn grain for ethanol controversial (Pimentel et al. 2009). A second-generation biofuel, cellulosic ethanol, has the potential to circumvent some of these problems by using plant residue (e.g. corn stover, wheat straw, or nonfood biomass) instead of corn grain (Service 2007; Ugarte et al. 2006). Still, further improvements to cellulosic ethanol production are necessary before it can become a viable substitution for grain ethanol. Finding biochemically labile feedstocks for cellulosic ethanol is a necessary step in this process. Agricultural ecosystems are also under pressure to increase their capacity to sequester soil organic matter (SOM), and this capacity is, in part, a function of the biochemical composition of the crop residue that remains after harvest. Here we consider the biochemical profiles of corn tissues from the perspectives of grain production, cellulosic ethanol production, and soil carbon sequestration.

Feedstock biochemical profiles influence the efficiency of cellulosic ethanol production, with high carbohydrate and low lignin levels being preferable (carbohydrate is the cellulosic ethanol feedstock; Sanchez and Cardona 2008). The lignin-hemicellulose copolymer is extremely difficult for enzymes and microbes to depolymerize and slows the conversion of carbohydrates into simple sugars (Hamelinck et al. 2005). To achieve the highest efficiency of conversion, lignin must be physically or chemically removed from biomass before fermentation (Sanchez and Cardona 2008). Current lignin management techniques include: improving biomass chemical processing (Sun and Cheng 2002; Wyman 2007), genetically altering enzymes to breakdown lignin (Zhang et al. 1995), and genetically engineering low-lignin plants (Sticklen 2008).

It has been assumed that cropping for both grain and residue (straw, stover, etc.) will require the same nutrient management practices as cropping exclusively for grain (e.g. Simpson et al. 2009). However, high levels of fertilizer application may not produce residues suitable for cellulosic ethanol production because N fertilization is unlikely to increase carbon (C) allocation equally to all plant tissues (i.e. grain, leaves, stems, and roots) and biochemicals (i.e. carbohydrate, protein, lignin, lipid). Previous studies have observed plant biochemical shifts in response to fertilization using biological assays and near-infrared spectroscopy. A typical response to N fertilization is increased protein and decreased carbohydrate concentrations (Zhang et al. 1993). Shifts in biomass allocation (e.g. from stems to roots) can also cause shifts in plant biochemical stocks since plant tissues each have a specific biochemical profile (Poorter and Bergkotte 1992; Poorter and Nagel 2000).

In addition to its effects on crop biochemistry, excess fertilization has negative environmental consequences (Carpenter et al. 1998; Bergstrom and Brink 1986; Power et al. 2000). N fertilizers are the main cause of hypoxic “dead zones” (Turner et al. 2008), and nitrate runoff into drinking water supplies has been linked to a number of health problems (Rao and Puttanna 2006). Furthermore, the use of synthetic fertilizers contributes to greenhouse gas emissions through 1) carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions during production (Wood and Cowie 2004) and 2) nonlinear increases in N_2O emissions from soils in response to the presence and cycling of inorganic N (McSwiney and Robertson 2005). Emissions of fossil fuel derived CO_2 and N_2O (GWP=310; Forster et al. 2007) from biofuel crop systems, can significantly reduce the climate benefits associated with the use of biofuels (Hill et al. 2009; Robertson et al. 2008). In this rapidly changing food and energy landscape, we must understand how to maximize crop yield while minimizing fertilizer application and energy consumption.

Our goal in this paper is to quantify the impact of N fertilization on biochemical yields in the whole-plant harvest of a conventional corn agricultural ecosystem. We hypothesize that corn grain and residue respond differently to N fertilization, with yields diminishing in response to fertilization. Because the metabolic pathway for plant lignin production requires phenolic amino acids, we also hypothesize that limiting N fertilization may be an effective way to reduce fuel feedstock lignin content. Finally, we recognize that plant nutrient status affects the decomposability of biomass, influencing the ability of soil to sequester C. Previous studies have considered only the effects of N fertilization on corn grain yield; here we additionally consider the effects of N fertilization on the quantity and quality of a potential cellulosic ethanol feedstock.

Site Description

We used corn grown at the Kellogg Biological Station –Long Term Ecological Research (KBS-LTER) Site (42°24'N, 85°24'W) in southwest Michigan during the 2006 growing season. For the year sampled (2006), KBS received 102.9 cm of precipitation and had a MAT=11.7 °C (KBS-LTER 2009). KBS soils are fine-loamy and coarse-loamy mixed, mesic Typic Hapludalfs (Crum and Collins 1995). Plants were fertilized with ammonium nitrate at seven rates (0, 34, 67, 101, 134, 168, and 202 kg N ha^{-1}), applied by hand in four replicate blocks (R1-R4; Fig. 20). The appropriate N fertilization rate for any particular agricultural ecosystem will depend on soil type, cropping history, and the crop being planted. For this field site, 0-67 kg N ha^{-1}, 101 kg N ha^{-1}, and 134-202 kg N ha^{-1} are characterized as deficient, sufficient, and excessive, respectively (McSwiney et al. 2010). All replicates were split into halves; one half with a winter wheat cover crop and the other without (Fig. 20; McSwiney et al. 2010). We present data on corn crops grown without a winter wheat cover crop. Corn plants were split into three tissue types: 1) grain, 2) reproductive support (husk, shank, tassel, and cob) and 3) leaf & stem (corn roots were not collected since roots are not typically harvested). Corn residue is the combination of the reproductive support and leaf and stem tissues. Further details on the field site design, sampling, and processing can be found in the in McSwiney et al. (2010).

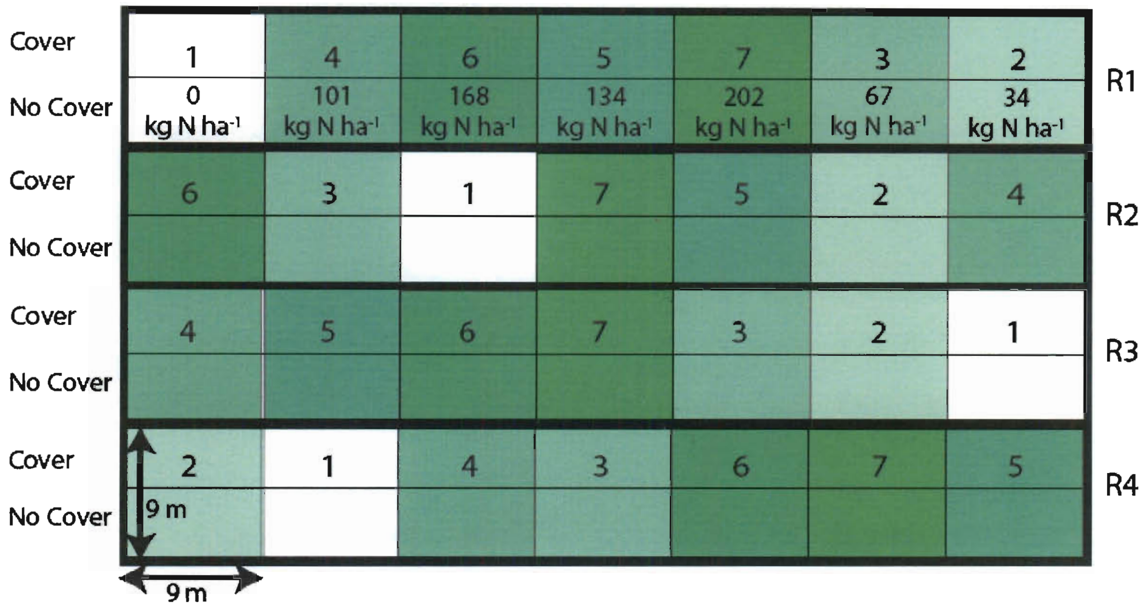

Figure 20. Experimental Design of the N Rate Experiment at KBS-LTER

Each N fertilization treatment was replicated in four (R1-R4) and split into a winter wheat cover crop and a no winter wheat cover crop treatment. Here we present results from replicate 1 through 4 of the no cover crop treatments for four of the seven fertilization rates (0, 67, 134, and 202 kg N ha^{-1}). Data was also collected for replicate 1 at the in-between fertilization rates (34, 101, and 168 kg N ha^{-1}).

Methods

We measured C and N concentrations using Costech 4010 and Perkin-Elmer 2400 series CHNS/O Elemental Analysis Systems (Appendix A3). We assessed carbohydrate, protein, lignin, and lipid concentrations using a rapid and accurate ^{13}C nuclear magnetic resonance (NMR) technique (Baldock et al. 2004; Nelson and Baldock 2005) developed for the organic geochemistry community (Hedges et al. 2001; Gelinas et al. 2001; Sanderman et al. 2008), but equally applicable to plant biochemical analyses. NMR has been recognized as a more accurate and effective technique for litter biochemical characterization (Harmon and Lajtha 1999) since studies in the late 1990s showed that wet extractive 'proximate' analyses often extracted materials chemically unrelated to the target compounds. For example, 'lignin' extractions have been shown to be enriched in cutins and tannins (Preston et al. 1997). Comparisons of wet chemical assays for lignin show differences of as much as 150% in yield (Hatfield and Fukushima 2005), pointing to the need to use modern analytical chemistry tools to assess plant biochemical composition. Solid-state ^{13}C NMR nondestructively quantifies organic chemical functional groups present in plant biochemicals (e.g. the phenolic functional groups present in lignin monomers), without chemical extraction or pretreatment. ^{13}C NMR is a robust method compared with other techniques, which are usually compound-specific and when combined, can detect as little as 20% of C present in a sample (Baldock et al. 2004; Harmon and Lajtha 1999).

Solid-state ^{13}C NMR spectra were collected on each corn tissue sample using a Bruker 200 MHz NMR. We performed cross polarization (CP) experiments using a 4mm magic angle spinning (MAS) probe spun at 5 kHz frequency, with a 1 ms contact time and a recycle delay >2 sec on all four replicates at fertilization rates 0, 67, 134, and 202 kg N ha^{-1} (Appendix D2). A single replicate (R1) was additionally analyzed at fertilization rates 34, 101, and 168 kg N ha^{-1}. The four replicates at 0, 67, 134 and 202 kg N ha^{-1} allow full error analysis, including instrumental variability as well as the natural variability of this agricultural site. All spectra were corrected for spinning side bands (SSB). We also spin-counted (Smernik and Oades 2001) each spectrum to quantitate the NMR data. An average of 77.7 ± 6.8% of the C was detected in the samples, and no spectrum detected less than 64.6% of the sample C. A cold (220°K) CP experiment was performed to determine if there was a systematic underdetection of mobile C structures (i.e. lipids). From this experiment we concluded all underdetection in observability is accounted for in mobile lipid structures (Fig. 21).

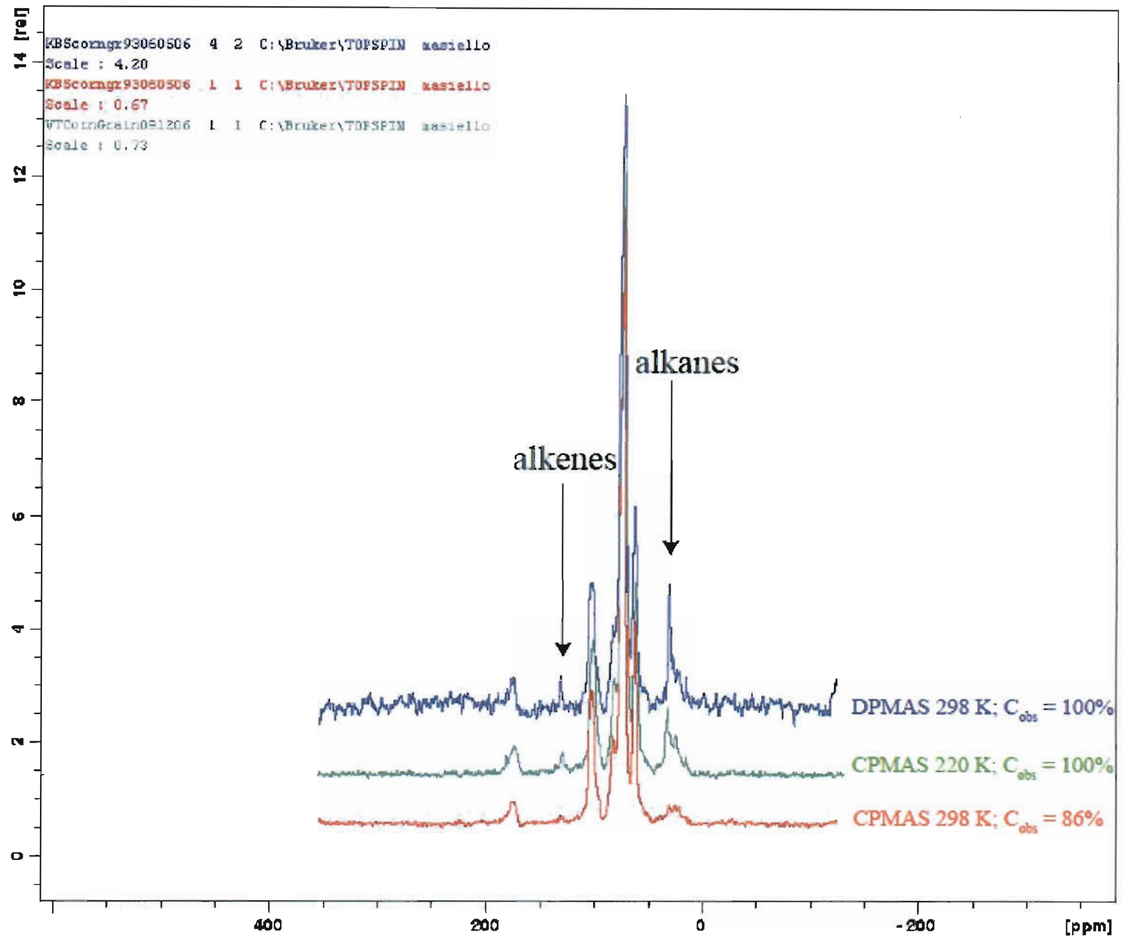

Figure 21. Carbon Observability, CP-MAS NMR Experiment

For the CP-MAS NMR experiments, an average 77.7 ± 6.8% of the C in the samples was detected. We performed CP-MAS NMR experiments on corn grain at cold temperature (220°K) to "freeze" the molecular motions of the chemical structures in the sample, and thereby increase the efficiency of the CP experiment. We observed an increase in signal intensity for spectral regions identified as alkanes and alkenes. Other regions of the spectrum were unaffected. The observability (C_{obs}) increased to 100% at 220°K as a result of more efficient polarization transfer to the mobile C in the lipid-like structures. Hence, all the underdetection in observability can be accounted for in lipids. Our analysis focuses on relative trends in carbohydrates and lignin in corn samples. Systematic NMR underdetection of lipid C has no effect on any of the results we report: relative rates of increase of carbohydrate and lignin.

To determine which C functionalities were systematically overdetected in the CP experiments, we collected direct polarization (DP) spectra on 14 samples (7 grain and 7 leaf & stem samples-Appendix E). All DP spectra were corrected for SSB and spin-counted, with an average of 87.8±19.2% C detected. DP pulse sequences are more accurate than CP; however, they are much noisier and often generate poorer quality spectra. To improve DP spectral quality, we collected DP spectra for 6x as long as CP spectra (12 versus 2 hrs per sample, respectively). This generated DP spectra of sufficient quality to determine that CP spectra overestimated carbohydrate yields by ~7%; less than natural variability noted between replicates for all but one of our samples. DP spectra did not yield recognizable peaks (above 3x noise) for the spectra regions used to calculate lipid, lignin, or protein concentrations, so we could not use DP spectra to generate these data. Because a linear offset of 7% for any of our data points has no effect on our results, we have chosen not to apply a correction factor to any results reported here.

^{13}C Nuclear Magnetic Resonance Spectroscopy and the Molecular Mixing Model

A molecular mixing model (MMM) was used to determine the biochemical composition of each corn biomass sample (Baldock et al. 2004; Nelson and Baldock 2005). The MMM uses a sample's C:N ratio and the signal distribution across seven predefined ^{13}C NMR spectral regions to calculate the relative abundance of four biochemical classes (carbohydrate, protein, lignin, and lipid; Appendix B2; Baldock et al. 2004; Nelson and Baldock 2005). The model simultaneously solves a suite of linear equations to divide each of the seven spectral regions of a sample into its biochemical components based upon the NMR spectra of standards that are representative of each biochemical class (e.g. cellulose for carbohydrate). Carbon-13 NMR experiments conducted in our lab using known mixtures of purified biopolymers indicate that the MMM results are accurate to ±1.0% (Table 9). Further validation of the MMM can be found in Nelson and Baldock (2005).

Table 9. C-13 NMR Molecular Mixing Model Precision and Accuracy

Results of CPMAS ^{13}C NMR experiments performed to determine the accuracy and precision of the MMM using a standard that was a mixture of pure cellulose and glycine. The theoretical values were calculated using the known mass ratio of the cellulose/glycine standard. MMM results are accurate to within ±1.0% as calculated with Eqn 12.

$$\text{Accuracy} = \frac{\text{Theoretical Value - Measured Value}}{\text{Theoretical Value}} * 100\% \qquad \text{Eqn. 12}$$

		Peak Area		MMM Estimates	
Analysis Date	Number of Scans	Cellulose Peak Area	Glycine Peak Area	Carbohydrate	Protein
09/03/07	500	52.8	46.3	53.0	47.0
10/04/07	16	52.0	46.7	51.5	48.5
10/12/07	1000	51.4	47.6	51.3	48.7
10/28/07	14000	50.8	48.2	50.9	49.1
11/12/07	1000	51.8	46.8	52.8	47.2
Theoretical (True) Value		52.4	47.6	52.4	47.6
Average		51.7	47.1	51.9	48.1
Standard Deviation		0.7	0.8	0.9	0.9
Precision (%RSD)		1.4%	1.6%	1.8%	2.0%
Accuracy (%Error)		***1.2%***	***-1.1%***	***1.0%***	***1.1%***

Calculations and Error

We used the MMM to determine the biomolecular content of three different corn tissue types over seven N fertilization rates (Appendix B). The percent composition of biochemicals in each sample, measured using ^{13}C NMR and the MMM, have errors of ±1%. Weighting the biomolecule mass percent with net primary production data (i.e. yield data Mg ha^{-1}; McSwiney et al. 2010) gives the total biochemical yield (carbohydrate, protein, lignin, or lipid; Table 10; Figs. 22-25) of the aboveground corn ecosystem (Eqn. 13).

$$\text{Biochemical Yield (Mg ha}^{-1}) = \text{Corn Tissue Yield (Mg ha}^{-1}) * \left[\frac{\text{Biochemical in Corn Tissue (\%)}}{100\%}\right] \qquad \text{Eqn. 13}$$

Natural variability is calculated as the standard deviation of replicates 1 through 4 for four fertilization rates. Biochemical yields for corn residue and the total plant for each replicate were calculated by summing the biochemical yields of their component tissues (e.g. Eqn. 14).

$$\text{Residue Lignin Yield (Mg ha}^{-1}) = \text{Leaf \& Stem} + \text{Reproductive Support Yields (Mg ha}^{-1}) \qquad \text{Eqn. 14}$$

Percent lignin, C and N for corn residue were calculated as the weighted averages of the component tissue (leaf and stem and reproductive support) values with the yield data (NPP) for each replicate (e.g. Eqn. 15), and these values were used to calculate environmental parameters (C:N, and lignin:N ratios) for the corn residue (Eqn. 16-17).

$$\%\ \text{Lignin}_{\text{residue}} = \frac{\%\text{Lignin}_{\text{Leaf\&Stem}} \cdot \text{NPP}_{\text{Leaf\&Stem}} + \%\text{Lignin}_{\text{Rep.Support}} \cdot \text{NPP}_{\text{Rep.Support}}}{\text{NPP}_{\text{Leaf\&Stem}} + \text{NPP}_{\text{Rep.Support}}} \qquad \text{Eqn. 15}$$

$$\text{C:N Ratio} = \frac{\text{Carbon (\% by mass)}}{\text{Nitrogen (\% by mass)}} \qquad \text{Eqn. 16}$$

$$\text{Lignin:N Ratio} = \frac{\text{Lignin (\% by mass)}}{\text{Nitrogen (\% by mass)}} \qquad \text{Eqn. 17}$$

Percent change in biochemical yield is the percent increase in biochemical yield at a particular fertilization rate when compared to the unfertilized plot and was calculated using Eqn. 18 (Table 11).

$$\text{Change (\%)} = \frac{[\text{Fertilized (Mg ha}^{-1}) - \text{Unfertilized Biochemical Yield (Mg ha}^{-1})]}{\text{Unfertilized Biochemical Yield (Mg ha}^{-1})} * 100\% \qquad \text{Eqn. 18}$$

Statistical analyses were performed using the data analysis tools in Microsoft Excel software. Statistical significance was determined using a two-tailed, t-test (two-sampled, unequal variance) to compare between fertilization rates for grain and residue biochemical yields, and environmental parameters (Appendix C4). A p-value of 0.05 was used as the significance threshold, above which results were not treated as statistically significant. Our complete data set, including statistical tables, can be found in the Appendices.

Results and Discussion

To determine the level of fertilizer application where yields of grain and corn residue ceased to increase significantly, we estimated biochemical yields (Mg ha^{-1}) for each plant tissue type for all four field replicates at fertilization rates 0, 67, 134, and 202 kg N ha^{-1} (Table 10; Figs. 22-25). Replicate 1 samples were analyzed at fertilization rates 34, 101, and 134 kg N ha^{-1} to clarify the trend between these rates.

Although we detected significant increases in total plant mass yields of carbohydrate with increased fertilization, carbohydrate yield from the corn residue changed only slightly in response to increased N fertilization (Table 10; Fig. 26), with maximum total carbohydrate yield (25% increase-Table 11) occurring at the highest fertilization rate (202 kg N ha^{-1}). The majority of the carbohydrate increase in the total plant occurs within the grain, which saw 73% of the increase in yield with 202 kg N ha^{-1}. Without fertilization, plant carbohydrate was dominated by residue carbohydrate (54%). When fertilized the dominant source of carbohydrate shifted to the grain (60%).

Table 10. Total Biochemical Yields

The absolute increases in total biochemical yields (Mg ha^{-1}) and error (natural variability) of carbohydrate, protein, lignin, and lipid for the corn tissues (grain, reproductive support, and leaf and stem), crop residue, and the total corn plant under seven different fertilization rates. Crop residue is the combination of the reproductive support and leaf & stem tissue. Rep 1 yield (Mg ha^{-1}) represents biochemical yields in replicate 1. Average yield (Mg ha^{-1}) represents the average biochemical yields for replicates 1, 2, 3, and 4 at the fertilization rates 0, 67, 134, and 202 kg N ha^{-1}. The error (Mg ha^{-1}) is the standard deviation for this average and represents the natural variability of this corn ecosystem. See Calculations and Error section for details.

		Carbohydrate (Mg ha^{-1})			Protein (Mg ha^{-1})			Lignin (Mg ha^{-1})			Lipid (Mg ha^{-1})		
	Fertilization Rate (kg N ha^{-1})	Rep 1 Yield	Average Yield	Error	Rep 1 Yield	Average Yield	Error	Rep 1 Yield	Average Yield	Error	Rep 1 Yield	Average Yield	Error
Corn Grain	0	3.12	3.53	0.41	0.17	0.21	0.04	0.19	0.22	0.04	0.08	0.07	0.03
	34	5.25			0.35			0.31			0.10		
	67	6.68	6.53	0.15	0.45	0.45	0.01	0.28	0.34	0.06	0.14	0.14	0.03
	101	6.47			0.49			0.44			0.09		
	134	6.95	7.17	0.38	0.49	0.54	0.05	0.38	0.36	0.02	0.12	0.15	0.06
	168	6.58			0.56			0.26			0.08		
	202	7.20	7.53	0.31	0.54	0.56	0.03	0.41	0.41	0.04	0.15	0.17	0.04
Reproductive Support	0	0.72	0.82	0.08	0.02	0.03	0.01	0.16	0.17	0.03	0.02	0.02	0.01
	34	0.87			0.03			0.20			0.01		
	67	0.98	1.04	0.04	0.04	0.03	0.00	0.24	0.24	0.01	0.02	0.02	0.01
	101	1.11			0.03			0.31			0.01		
	134	1.38	1.17	0.18	0.04	0.04	0.01	0.29	0.24	0.04	0.02	0.02	0.01
	168	1.14			0.04			0.26			0.04		
	202	1.10	1.26	0.13	0.03	0.04	0.01	0.23	0.29	0.04	0.03	0.02	0.01
Leaf & Stem	0	2.85	3.27	0.44	0.08	0.10	0.03	0.56	0.77	0.14	0.12	0.12	0.03
	34	3.22			0.13			0.83			0.12		
	67	3.63	3.49	0.12	0.19	0.17	0.02	0.93	0.87	0.06	0.12	0.13	0.02
	101	3.10			0.20			0.71			0.19		
	134	3.58	3.57	0.27	0.18	0.23	0.04	0.95	0.92	0.08	0.11	0.15	0.05
	168	3.29			0.22			0.82			0.10		
	202	3.98	3.85	0.14	0.27	0.28	0.02	0.98	1.03	0.05	0.17	0.17	0.04
Crop Residue	0	3.57	4.09	0.51	0.10	0.13	0.03	0.72	0.94	0.15	0.14	0.14	0.03
	34	4.09			0.16			1.03			0.13		
	67	4.61	4.53	0.09	0.23	0.20	0.02	1.17	1.11	0.07	0.14	0.15	0.01
	101	4.22			0.23			1.02			0.20		
	134	4.96	4.74	0.40	0.22	0.27	0.05	1.24	1.16	0.10	0.12	0.18	0.05
	168	4.43			0.26			1.08			0.13		
	202	5.08	5.11	0.18	0.30	0.32	0.03	1.21	1.32	0.09	0.20	0.19	0.05
Total Corn Plant	0	6.69	7.62	0.90	0.26	0.34	0.07	0.91	1.16	0.17	0.21	0.21	0.05
	34	9.34			0.51			1.34			0.22		
	67	11.29	11.1	0.17	0.68	0.65	0.03	1.46	1.45	0.04	0.29	0.28	0.03
	101	10.69			0.72			1.46			0.29		
	134	11.91	11.9	0.67	0.71	0.80	0.10	1.62	1.52	0.12	0.25	0.33	0.10
	168	11.02			0.82			1.34			0.22		
	202	12.28	12.6	0.42	0.84	0.88	0.05	1.61	1.73	0.10	0.35	0.36	0.08

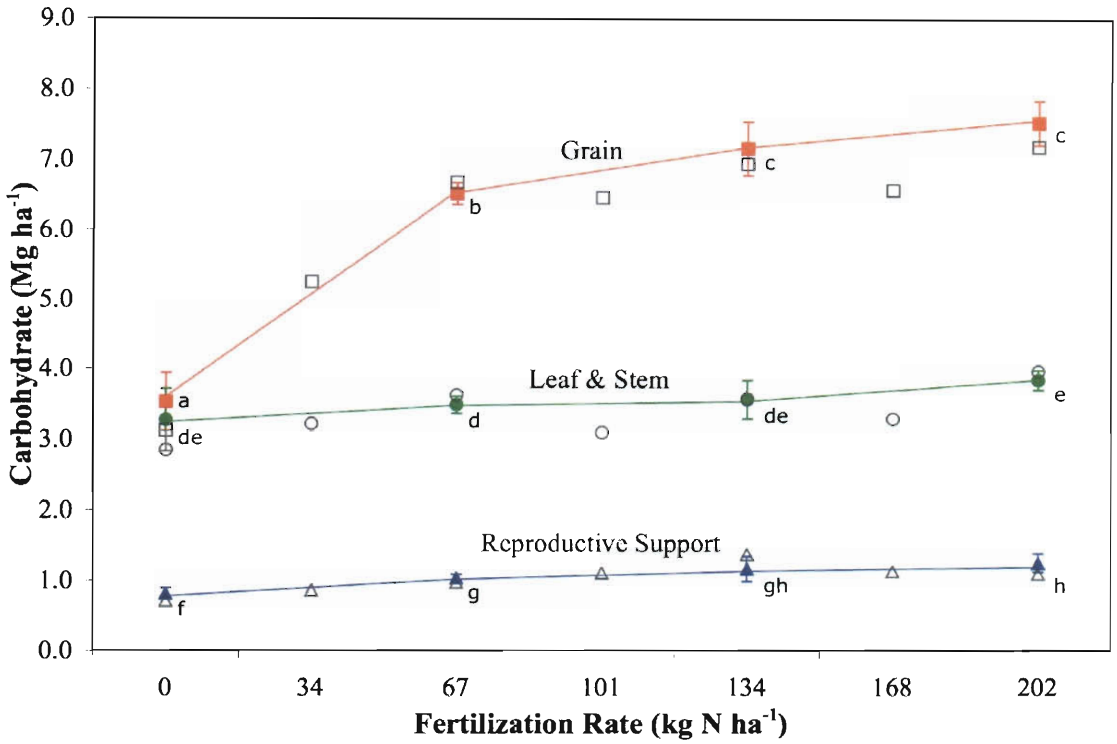

Figure 22. Total Carbohydrate Stocks for Each Tissue Type

The change in total carbohydrate stock yields for grain, leaf and stem, and reproductive support in Mg ha^{-1} over seven N fertilization rates. The color symbols (red square-grain, blue triangle-reproductive support, and green circle-leaf & stem) represent the average of replicates 1 through 4 for the biochemical yield at four fertilization rates (0, 67, 134, 202 kg N ha^{-1}). Natural variability is the standard deviation of the biochemical stocks for replicates 1 through 4 at these four fertilization rates and is represented by the error bars on these yields. Open squares, triangles, and circles represent grain, reproductive support, and leaf and stem replicate 1 data, respectively. Different letters, or combination of letters, represent stocks that are significantly different from each other (two-tailed t-test; p-value<0.05; Appendix C).

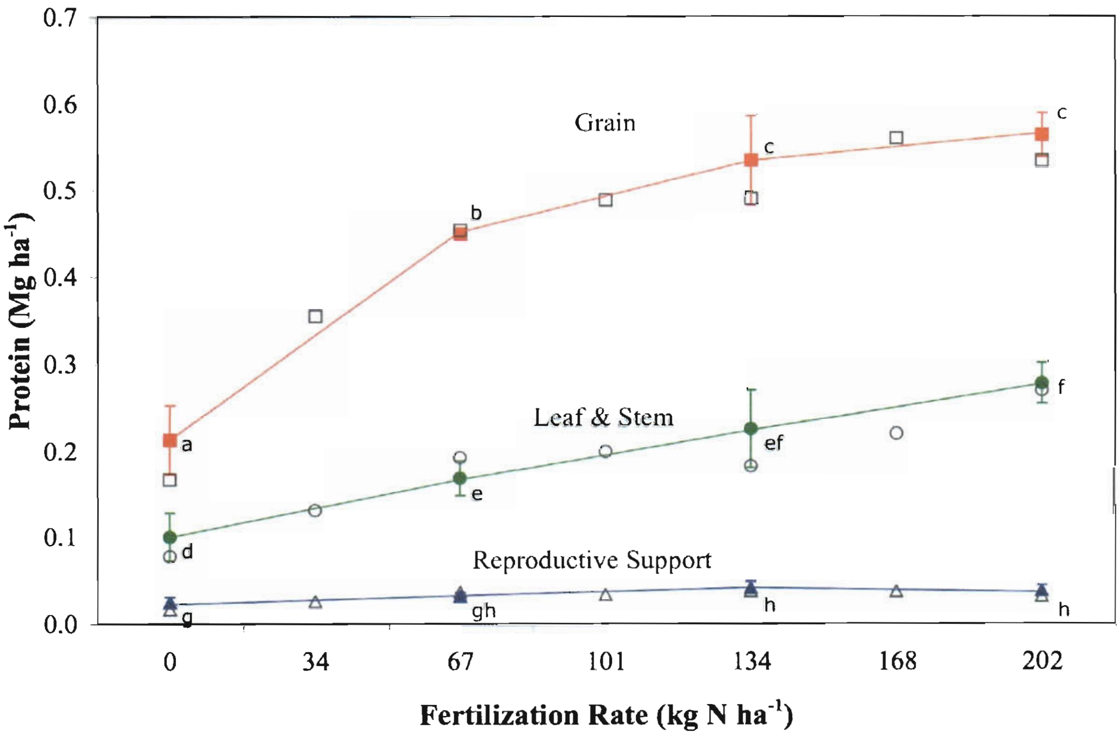

Figure 23. Total Protein Stocks for Each Tissue Type

The change in total protein stock yields for grain, leaf and stem, and reproductive support in Mg ha^{-1} over seven N fertilization rates. The color symbols (red square-grain, blue triangle-reproductive support, and green circle-leaf & stem) represent the average of replicates 1 through 4 for the biochemical yield at four fertilization rates (0, 67, 134, 202 kg N ha^{-1}). Natural variability is the standard deviation of the biochemical stocks for replicates 1 through 4 at these four fertilization rates and is represented by the error bars on these yields. Open squares, triangles, and circles represent grain, reproductive support, and leaf and stem replicate 1 data, respectively. Different letters, or combination of letters, represent stocks that are significantly different from each other (two-tailed t-test; p-value<0.05; Appendix C).

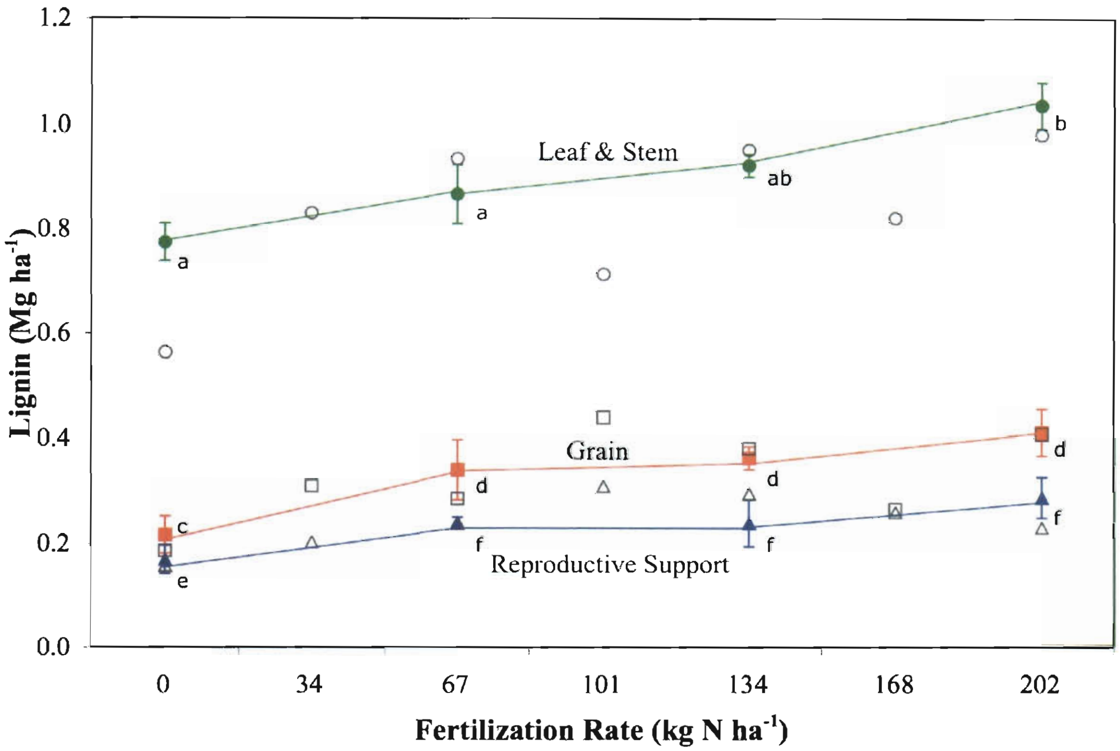

Figure 24. Total Lignin Stocks for Each Tissue Type

The change in total lignin stock yields for grain, leaf and stem, and reproductive support in Mg ha^{-1} over seven N fertilization rates. The color symbols (red square-grain, blue triangle-reproductive support, and green circle-leaf & stem) represent the average of replicates 1 through 4 for the biochemical yield at four fertilization rates (0, 67, 134, 202 kg N ha^{-1}). Natural variability is the standard deviation of the biochemical stocks for replicates 1 through 4 at these four fertilization rates and is represented by the error bars on these yields. Open squares, triangles, and circles represent grain, reproductive support, and leaf and stem replicate 1 data, respectively. Different letters, or combination of letters, represent stocks that are significantly different from each other (two-tailed t-test; p-value<0.05; Appendix C).

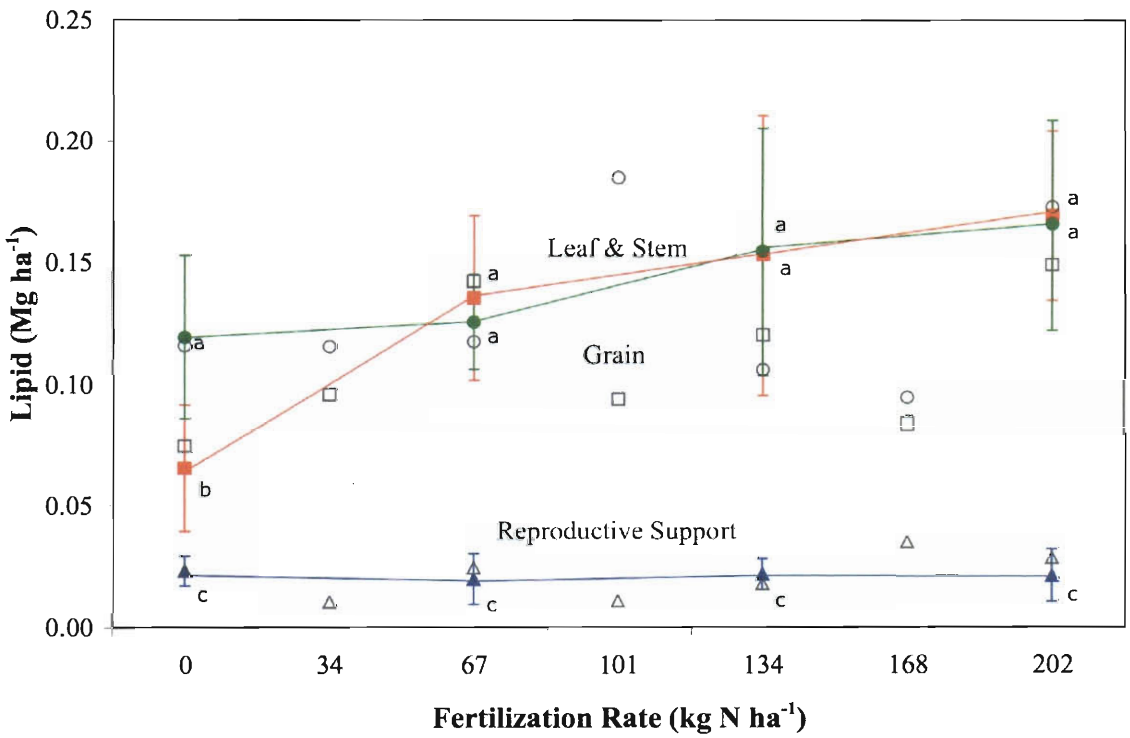

Figure 25. Total Lipid Stocks for Each Tissue Type

The change in total lipid stock yields for grain, leaf and stem, and reproductive support in Mg ha^{-1} over seven N fertilization rates. The color symbols (red square-grain, blue triangle-reproductive support, and green circle-leaf & stem) represent the average of replicates 1 through 4 for the biochemical yield at four fertilization rates (0, 67, 134, 202 kg N ha^{-1}). Natural variability is the standard deviation of the biochemical stocks for replicates 1 through 4 at these four fertilization rates and is represented by the error bars on these yields. Open squares, triangles, and circles represent grain, reproductive support, and leaf and stem replicate 1 data, respectively. Different letters, or combination of letters, represent stocks that are significantly different from each other (two-tailed t-test; p-value<0.05; Appendix C). Lipid concentrations are difficult to constrain using ^{13}C NMR and the MMM due to their high molecular mobility.

Table 11. Percent Change in Total Biochemical Yields

The percent change in total yields of each biochemical with the addition of either 67 kg N ha^{-1}, 134 kg N ha^{-1}, or 202 kg N ha^{-1} of N fertilizer compared to the biochemical yields of the unfertilized plots, calculated using Eqn. 18. Asterisks represent values that are significant changes from the unfertilized plot based on different p-values for a two-tailed t-test (*p-value<0.05; **p-value<0.01; ***p-value<0.001; ****p-value<0.0001; ^p-value <0.1; Appendix C).

		Increase with Nitrogen Fertilization				
		Grain	**Reproductive Support**	**Leaf & Stem**	**Crop Residue**	**Total Plant**
67 kg N ha^{-1}	Carbohydrate	85%***	27%**	7%	11%	45%**
	Protein	111%**	27%^	68%**	60%**	92%**
	Lignin	57%*	43%**	12%	17%	25%*
	Lipid	106%*	-14.0%	5%	2%	35%^
134 kg N ha^{-1}	Carbohydrate	103%****	43%*	9%	16%^	56%***
	Protein	151%****	64%*	125%**	113%**	137%***
	Lignin	67%**	41%*	19%	23%^	31%*
	Lipid	133%*	-5%	30%	24%	58%^
202 kg N ha^{-1}	Carbohydrate	114%****	54%**	18%^	25%*	66%***
	Protein	165%****	52%*	177%****	152%***	160%****
	Lignin	89%***	70%**	34%*	40%**	49%**
	Lipid	158%**	-6%	39%	32%	72%*

For grain production, both carbohydrate and protein respond non-linearly to N fertilization, plateauing between 67 and 134 kg N ha^{-1} (Fig. 26a; Fig. 26b). Increasing fertilization rates from 134 to 202 kg N ha^{-1} does not increase grain yield for either carbohydrate or protein (p-values = 0.189 and 0.405, respectively). Increasing fertilization from 67 to 134 kg N ha^{-1} only increases grain carbohydrate yields by 0.64 Mg ha^{-1} (a 10% increase; p-value = 0.034); small compared to the 85% increase in yield between 0 and 67 kg N ha^{-1} (p-value=0.0002).

For corn residue, carbohydrate yield (the majority of cellulosic ethanol feedstock) responded slowly to N fertilization. Carbohydrate yields in the corn residue at fertilization rates 0, 67, and 134 kg N ha^{-1} were all statistically the same (Table 10; p-values >0.09). Carbohydrate yields at low fertilization rates (0 and 67 kg N ha^{-1}) were lower than yields at the highest fertilization rate of 202 kg N ha^{-1} (p-values = 0.022 and 0.004, respectively). Corn residue carbohydrate yields at the high fertilization rates, 134 and 202 kg N ha^{-1}, were statistically indistinguishable (p-value = 0.160). Even at the highest fertilization rate, the crop residue only responded with a 25% increase in carbohydrate yield (Table 11).

In combination, the grain and residue data imply a fertilization threshold between 67 and 134 kg N ha^{-1} beyond which yield returns are not likely to justify the cost of additional fertilizer, regardless of the biochemical desired (carbohydrate for fuel or protein for food). When the trends in Fig. 26a and Fig. 26b (based upon the analysis of a single replicate (R1)) are considered we can speculate that the threshold is closer to 67 kg N ha^{-1} than 134 kg N ha^{-1}.

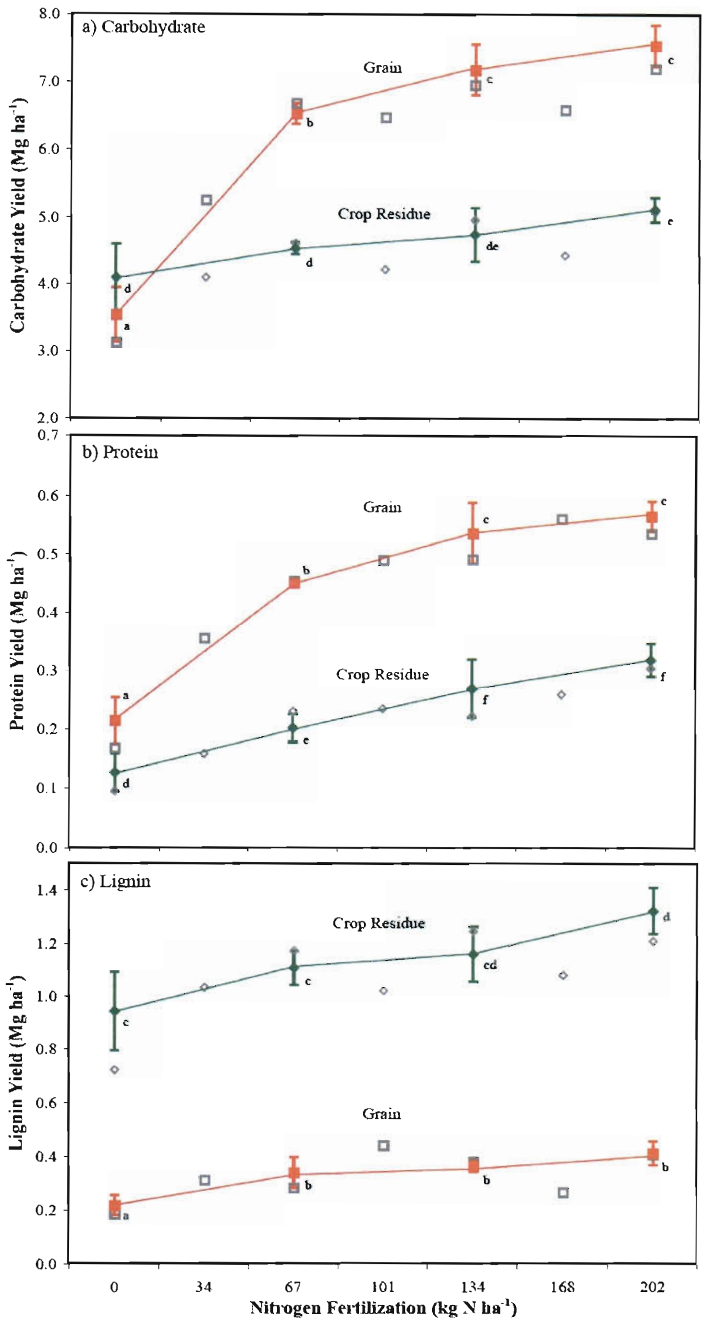

Figure 26. Corn Grain and Crop Residue Biochemical Stocks

Variations in biochemical yields with increasing N fertilization rates: a) carbohydrate, b) protein, and c) lignin stocks. The solid symbols (red square-grain, and green diamond-corn residue), connected with black lines, represent the average of replicates 1 through 4 for the biochemical yield at four fertilization rates (0, 67, 134, 202 kg N ha^{-1}). Natural variability is the standard deviation of the biochemical stocks for replicates 1, 2, 3, and 4 at these four fertilization rates and is represented by the error bars on these yields. Different letters, or combination of letters, represent biochemical stocks that are significantly different from each other (two-tailed t-test; p-value < 0.05 – Appendix C). The open grey symbols represent replicate 1 data.

If crops are grown for cellulosic ethanol, plant lignin content must also be considered. In cellulosic ethanol production, feedstock carbohydrate (primarily cellulose) is depolymerized into a mixture of simple sugars, which microbial fermentation then converts to ethanol (Sanchez and Cardona 2008). Plant lignin content influences cellulosic ethanol production efficiency. Lignin is extremely resistant to hydrolytic enzymes and slows the conversion of cellulose and hemicellulose to simple sugars (Hamelinck et al. 2005). To achieve the highest efficiency of conversion, lignin must be physically or chemically removed from plant biomass before fermentation (Sanchez and Cardona 2008). Current approaches to reducing lignin recalcitrance include: improving biomass chemical processing (Sun and Cheng 2002; Wyman 2007), genetically altering enzymes to breakdown lignin (Zhang et al. 1995), and genetically engineering low-lignin plants (Sticklen 2008). Below, our results suggest that the precise management of N fertilization (i.e. precision agriculture) may also be an effective way to reduce fuel feedstock lignin content (Fig. 26c).

When fertilized, corn residue lignin yield increased by 17-40%, while carbohydrate yield only increased by 11-25% (Table 11; Fig. 26c; Fig. 26a). Fertilizing at a low rate, 67 kg N ha^{-1}, did not significantly increase carbohydrate yields (11%; 0.44 Mg ha^{-1}; p-value =0.179), or lignin yields (17%; 0.17 Mg ha^{-1}; p-value=0.097). Applying a high fertilization rate (202 kg N ha^{-1}) increased carbohydrates by 25% (1.02 Mg ha^{-1}; p-value=0.022), while lignin increased 40% (0.38 Mg ha^{-1}; p-value =0.006). The increase in lignin yield with fertilization (17-40% increase-Table 11) is likely due to the dependence of lignin biosynthesis upon the availability of aromatic amino acid precursors (phenylalanine and tyrosine; van Rensburg et al. 2000). Phenylalanine availability is rate-limiting in lignin biosynthesis at the cellular level (van Rensburg et al. 2000). With the addition of fertilizer at even the lowest rate (34 kg N ha^{-1}), lignin production is stimulated as plant N requirements are met (Fig. 26c). Hence, over-fertilization could produce a less biochemically favorable cellulosic ethanol feedstock, since crop residue lignin increases more rapidly than carbohydrate in response to N. There may be potential for fertilizer management to improve efficiency of cellulosic ethanol production through controlling plant lignin production.

To assess sustainability of the entire biofuel cropping system, soil C must also be considered. If all corn residues are not harvested as feedstock for cellulosic ethanol, some can be left in the field to build SOM. Maintaining SOM is critical to sustainability as organic matter maintains soil moisture, retains nutrients, and supports beneficial microbiota and invertebrates (Tiessen et al. 1994). Slower decomposition of residue allows for SOM to accumulate and this is influenced by litter biochemistry (Singh and Gupta 1977; Melillo et al. 1982; Melillo et al. 1989). Two parameters used to predict decomposition rates are C:N and lignin: N ratios (Melillo et al. 1989; Johnson et al. 2007). Higher C:N and lignin:N ratios indicate that the residue will have slower decomposition rates in soil (Singh and Gupta 1977; Johnson et al. 2007; Melillo et al. 1982). Residue N content influences decomposition rates, since microbes use N for cell growth. At our site, the highest plant C:N and lignin:N ratios, best for soil C storage, occur at the lowest fertilization levels (Fig. 27a; Fig. 27b; Fig. 28). As N fertilization increases, the corn residue becomes easier for microbes to decompose, allowing more residue C to be oxidized to CO_2 and released to the atmosphere rather than stored in soil. In a C-based economy, this would create further disincentives to over-fertilization.

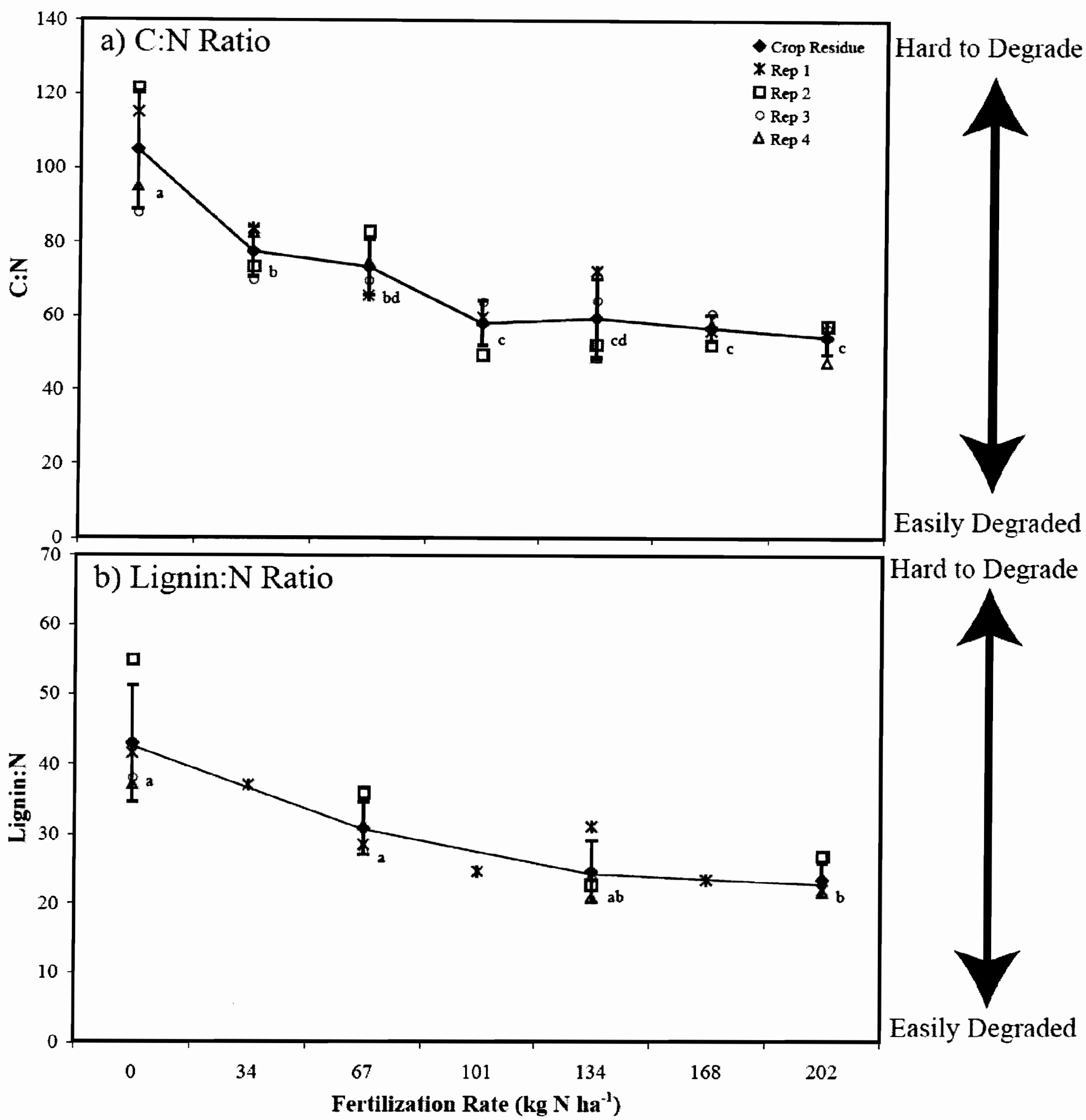

Figure 27. Indicators of Environmental Recalcitrance

The parameters a) C:N ratios and b) lignin:N ratios are indicators of biomass decomposability in the soil. Different letters, or combination of letters, represent ratios that are significantly different from each other (two-tailed t-test; p-value < 0.05 – Appendix C). For cropping systems that harvest part of crop residues for cellulosic ethanol production and leave some residue in the soil, low fertilization rates produce residues that convert more efficiently to ethanol and also generate more stable organic matter if left in the soil.

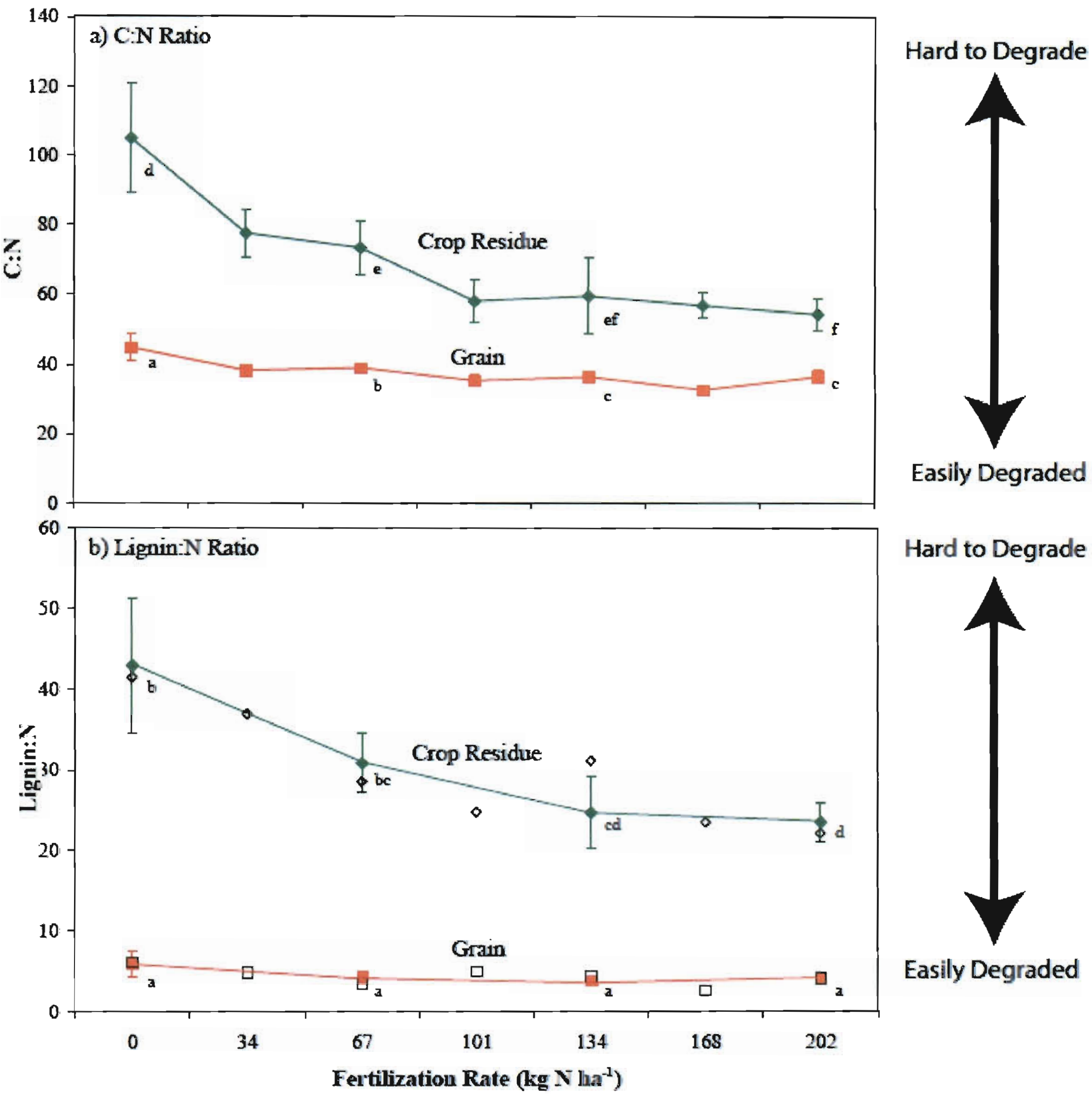

Figure 28. Corn Grain versus Crop Residue Environmental Indices

Environmental indices for the grain (red and open squares) and crop residue (green and open diamonds) over seven N fertilization rates; a) C:N ratios and b) lignin:N ratios are indicators of biomass decomposability. Different letters, or combination of letters, represent stocks that are significantly different from each other (two-tailed t-test; p-value<0.05; Appendix C).

Table 12. Fertilizer Nitrogen Use Efficiency (FUE) in Biofuel Crops

A comparison of Fertilizer Nitrogen Use Efficiency (FUE) across a N gradient for two biofuel crops: corn and switchgrass. FUE is calculated using Eqn. 19. a)-corn FUE data for the N rate experiment is calculated using total yield data from McSwiney et al. 2009 . b)-switchgrass FUE data is from Lemus et al. 2008 .

$$\text{FUE} = \frac{\text{Nitrogen Fertilized Yield (Mg ha}^{-1}\text{)} - \text{Unfertilized Yield (Mg ha}^{-1}\text{)}}{\text{Nitrogen applied (kg N ha}^{-1}\text{)}} \cdot 100 \quad \text{Eqn. 19}$$

Nitrogen Fertilization Rate	Fertilizer Nitrogen Use Efficiency (FUE)					
(kg N ha^{-1})	Corn Grain[a]	Corn Reproductive Support[a]	Corn Leaf & Stem[a]	Crop Residue[a]	Total Corn[a]	Switchgrass[b]
0	~	~	~		~	~
34	5.23	0.30	0.15	0.45	**5.68**	NA
56	NA	NA	NA	NA	NA	**2.00**
67	5.11	0.45	0.58	1.02	**6.14**	NA
101	3.92	0.42	0.33	0.75	**4.67**	NA
112	NA	NA	NA	NA	NA	**1.50**
134	3.13	0.33	0.45	0.78	**3.91**	NA
168	2.53	0.35	0.37	0.72	**3.24**	NA
202	2.30	0.28	0.53	0.81	**3.12**	NA
224	NA	NA	NA	NA	NA	**0.85**

Conclusions

We show that crop biochemical profiles can be managed, in part, by altering N fertilization rates, and that optimizing agricultural practices for carbohydrate yields may reduce the environmental impact of cellulosic ethanol production. However, before large-scale introduction of this process, other issues need attention. Plant response to N fertilization varies within and between species (Table 12), likely leading to significant diversity in plant biochemical yield. Our approach to optimizing biochemical yields will need to be tested in other viable cellulosic biofuel crops (e.g. switchgrass) before our results can be extrapolated to other agrisystems. In addition, it will be very important to determine the effects of residue harvesting practices on soil erosion, sustainability of soil C pools, and net agricultural greenhouse gas balances.

CHAPTER 4

A Cost Assessment of the Effects of Sustainable Agriculture Techniques on Corn Crop Biochemical Yields

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In Preparation for

Agriculture, Ecosystems, and Environment

Abstract

Sustainable agriculture practices, such as cover crops and precision N management, can help meet food and energy industry needs in the long-term. C-13 nuclear magnetic resonance spectroscopy can improve precision agriculture techniques by allowing farmers to crop for specific biochemicals (e.g. protein or carbohydrate) depending on the intended crop use (i.e. food or biofuel). This is possible since ^{13}C NMR can estimate crop carbohydrate, protein, lignin, and lipid yields. Here we measure biochemical stocks of a corn ecosystem under different cover crop conditions and different levels of N fertilization. To assess whether the use of a cover crop or increased fertilizer results in increasing yields, we perform a simple cost assessment using 2006 agriculture production costs. We found that N fertilization is the main control on corn biochemical and mass yields. The use of a cover crop has no significant impact on corn biochemical yields except when no fertilizer is applied. Cropping for protein or carbohydrate in corn grain is most cost-effective at slightly higher N fertilization rates, 101-134 and ~134 kg N ha^{-1}, respectively, while cropping residue for carbohydrate is more cost-effective at lower N fertilization rates, 67 kg N ha^{-1}. Even without any consideration of environmental costs (e.g. dead zones, groundwater pollution) it is not financially advantageous to apply fertilizer at high levels, while the minor costs and environmental benefits of using a cover crop make its use beneficial.

Introduction

Increasing population projections have created concerns about food, water, land, and energy shortages (Spiertz 2010). These concerns have led to increased pressure on ecosystems and the agricultural industry. Agriculture ecosystems are major consumers of water, land, and energy and are critical to the food and, in recent years, energy industries, due to demand for biofuels (Solomon et al. 2007). Sustainable agriculture techniques, by definition, have the potential to meet the food and energy industries' needs, while reducing environmental impacts (Cassman and Liska 2007; Lichtfouse et al. 2009; Spiertz 2010; Matson et al. 1997).

Environmental Impacts of Agriculture

Agriculture focuses on manipulating land for production, which can have significant environmental impacts (Hazell and Wood 2008). Land use change, soil tilling, use of farm machinery, and fertilizer and pesticide production can all lead to environmental degradation (Robertson and Grace 2004; Houghton and Goodale 2004). For example, cropping has led to increased soil erosion, and has also decreased soil organic carbon (C) accumulation (Grandy and Robertson 2007; Ortega et al. 2002; Tiessen et al. 1994). Excessive use of nitrogen (N) fertilizers leads to nitrate (NO_3^-) runoff (Bergstrom and Brink 1986; Power et al. 2000) and is recognized to be the main cause of hypoxic 'dead zones' in the Gulf of Mexico (Burkart and James 1999; Turner et al. 2008; Rabalais et al. 2007) and worldwide (Diaz and Rosenberg 2008). Nitrate runoff into groundwater supplies has also been linked to numerous health problems (Rao and Puttanna 2006). Furthermore, the use of synthetic fertilizers contributes to greenhouse gas emissions through carbon dioxide (CO_2 – GWP: 1), methane (CH_4 – GWP: 21), and nitrous oxide (N_2O – GWP: 310) emissions during fertilizer production and use during cropping (Forster et al. 2007; Wood and Cowie 2004). N_2O emissions from soils respond nonlinearly to increasing N fertilization rates, increasing rapidly once plant N needs are met (McSwiney and Robertson 2005).

Sustainable Agriculture

The environmental impacts of the agricultural industry have led to increased efforts to develop sustainable management techniques to minimize them at the local- to global-scale. Sustainable agriculture takes into consideration economics, society, and the environment in crop management decisions (Robertson and Swinton 2005; Robertson et al. 2008; Spiertz 2010; Lichtfouse et al. 2009). Management techniques used to improve agricultural sustainability include use of cover crops, not tilling soils, reduction of N inputs, and organic practices (Drinkwater and Snapp 2007; Snapp et al. 2005; Spiertz 2010). Practices that improve sustainability can prolong crop grain and crop residue yields over the long-term (Ugarte et al. 2006).

Cover Crop

The use of a cover crop can have both environmental and economic benefits. A cover crop can be used as an agriculture management technique to reduce soil erosion, increase soil N availability (e.g. N-fixing cover crops, N immobilization), reduce pests and disease or increase crop yield (as reviewed in Snapp et al. 2005). Many cover crops can also be sold as a secondary cash crop. Some cover crops can be used to immobilize N (remove soil N and store in biomass) during fallow, to be released back into the soil prior to planting (McSwiney et al. 2010), in effect, acting as a slow-release fertilizer to prevent watershed pollution.

Results and Discussion

Biochemical Stocks

Cover Crop

The addition of a cover crop has no impact on biochemical yield regardless of level of N fertilization in corn crop residue (Table 14; Fig. 31). The use of a cover crop does not affect carbohydrate, protein, or lignin yields in corn grain when the crop is receiving fertilizer. When unfertilized, cover crop treatments had slightly lower grain carbohydrate and protein yields than crops grown with a cover crop (Fig. 31a; Fig. 31c). This is due to N immobilization by the winter wheat cover crop. Since N is not readily available for plant use and there is no external N source (i.e. fertilizer), plant biochemical production is limited.

Nitrogen Fertilization

Biochemical stocks in corn grain respond strongly to N fertilization, particularly carbohydrate and protein (Gallagher et al. In Review). Both grain carbohydrate and protein respond nonlinearly to increasing N fertilization whether grown with or without a cover crop (Fig. 31a; Fig. 31b). However, there is little change in grain lignin and lipid stocks (Fig. 31c; Fig 31d). Crop residue stocks respond linearly to N fertilization, specifically carbohydrate, protein, and lignin stocks (Fig 31c; Fig. 31f; Fig. 31g). There are no observable changes in lipid stocks with N fertilization in the grain or crop residue (Fig. 31d; Fig. 31h).

Table 14. The Effects of Agricultural Management Techniques on Biochemical Stocks

Biochemical stocks of carbohydrate, protein, lignin, and lipid for corn grain, reproductive support, leaf and stem, residue, and total plant grown under varying N fertilization and cover crop treatments. Error represents the natural variability between Reps 1-4 (standard deviation). Values at fertilization rates 0, 67, 134, and 202 kg N ha^{-1} are averages of stocks for Reps 1-4. Values at fertilization rates 34, 101, and 168 kg N ha^{-1} are for Rep 1. Fertilization rate significantly impacts biochemical yields, while the addition of a cover crop has minimal, if any, impacts.

		Carbohydrate (Mg ha^{-1})				Protein (Mg ha^{-1})				Lignin (Mg ha^{-1})				Lipid (Mg ha^{-1})			
		No Cover Crop		Cover Crop		No Cover Crop		Cover Crop		No Cover Crop		Cover Crop		No Cover Crop		Cover Crop	
	Fertilization Rate (kg N ha^{-1})	Yield	Error	Yield	Error	Yield	Error	Yield	Error	Yield	Error	Yield	Error	Yield	Error	Yield	Error
Corn Grain	0	3.53	0.41	2.57	0.41	0.21	0.04	0.16	0.01	0.22	0.04	0.14	0.02	0.07	0.03	0.04	0.03
	34	5.25		4.87		0.35		0.30		0.31		0.26		0.10		0.13	
	67	6.53	0.15	6.29	0.61	0.45	0.01	0.42	0.06	0.34	0.06	0.27	0.05	0.14	0.03	0.15	0.04
	101	6.47		6.29		0.49		0.43		0.44		0.40		0.09		0.10	
	134	7.17	0.38	7.46	0.32	0.54	0.05	0.61	0.08	0.36	0.02	0.30	0.10	0.15	0.06	0.12	0.04
	168	6.47		7.39		0.56		0.54		0.26		0.39		0.08		0.20	
	202	7.53	0.31	7.24	0.52	0.56	0.03	0.61	0.02	0.41	0.04	0.39	0.06	0.17	0.04	0.17	0.06
Reproductive Support	0	0.82	0.08	0.73	0.07	0.03	0.01	0.02	0.01	0.17	0.03	0.16	0.02	0.02	0.01	0.02	0.00
	34	0.87		0.94		0.03		0.03		0.20		0.22		0.01		0.02	
	67	1.04	0.04	1.14	0.10	0.03	0.00	0.04	0.01	0.24	0.01	0.25	0.03	0.02	0.01	0.02	0.01
	101	1.11		1.20		0.03		0.04		0.31		0.24		0.01		0.03	
	134	1.17	0.18	1.32	0.08	0.04	0.01	0.05	0.01	0.24	0.04	0.26	0.02	0.02	0.01	0.02	0.01
	168	1.14		1.37		0.04		0.04		0.26		0.27		0.04		0.04	
	202	1.26	0.13	1.30	0.07	0.04	0.01	0.05	0.01	0.29	0.04	0.30	0.03	0.02	0.01	0.03	0.01
Leaf & Stem	0	3.27	0.44	2.70	0.21	0.10	0.03	0.09	0.01	0.77	0.14	0.66	0.16	0.12	0.03	0.08	0.05
	34	3.22		3.24		0.13		0.13		0.83		0.90		0.12		0.06	
	67	3.49	0.12	3.37	0.15	0.17	0.02	0.17	0.03	0.87	0.06	0.86	0.09	0.13	0.02	0.12	0.03
	101	3.10		3.35		0.20		0.17		0.71		0.72		0.19		0.18	
	134	3.57	0.27	3.51	0.17	0.23	0.04	0.25	0.04	0.92	0.08	0.84	0.11	0.15	0.05	0.15	0.04
	168	3.29		3.84		0.22		0.27		0.82		0.81		0.10		0.19	
	202	3.85	0.14	3.60	0.22	0.28	0.02	0.26	0.02	1.03	0.05	0.90	0.03	0.17	0.04	0.16	0.06
Crop Residue	0	4.09	0.51	3.43	0.27	0.13	0.03	0.11	0.01	0.94	0.15	0.83	0.17	0.14	0.03	0.10	0.05
	34	4.09		4.18		0.16		0.16		1.03		1.11		0.13		0.08	
	67	4.53	0.09	4.51	0.19	0.20	0.02	0.21	0.04	1.11	0.07	1.10	0.10	0.15	0.01	0.14	0.02
	101	4.22		4.55		0.23		0.20		1.02		0.96		0.20		0.20	
	134	4.74	0.40	4.83	0.17	0.27	0.05	0.30	0.04	1.16	0.10	1.10	0.11	0.18	0.05	0.18	0.05
	168	4.43		5.21		0.26		0.31		1.08		1.08		0.13		0.23	
	202	5.11	0.18	4.91	0.25	0.32	0.03	0.31	0.01	1.32	0.09	1.19	0.06	0.19	0.05	0.19	0.06
Total Corn Plant	0	7.62	0.90	6.00	0.57	0.34	0.07	0.27	0.02	1.16	0.17	0.97	0.18	0.21	0.05	0.14	0.06
	34	9.34		9.05		0.51		0.46		1.34		1.38		0.22		0.22	
	67	11.1	0.17	10.80	0.80	0.65	0.03	0.63	0.09	1.45	0.04	1.37	0.11	0.28	0.03	0.29	0.04
	101	10.69		10.84		0.72		0.64		1.46		1.37		0.29		0.30	
	134	11.9	0.67	12.29	0.40	0.80	0.10	0.91	0.11	1.52	0.12	1.40	0.09	0.33	0.10	0.29	0.05
	168	11.02		12.60		0.82		0.84		1.34		1.47		0.22		0.44	
	202	12.6	0.42	12.15	0.74	0.88	0.05	0.92	0.03	1.73	0.10	1.58	0.09	0.36	0.08	0.36	0.12

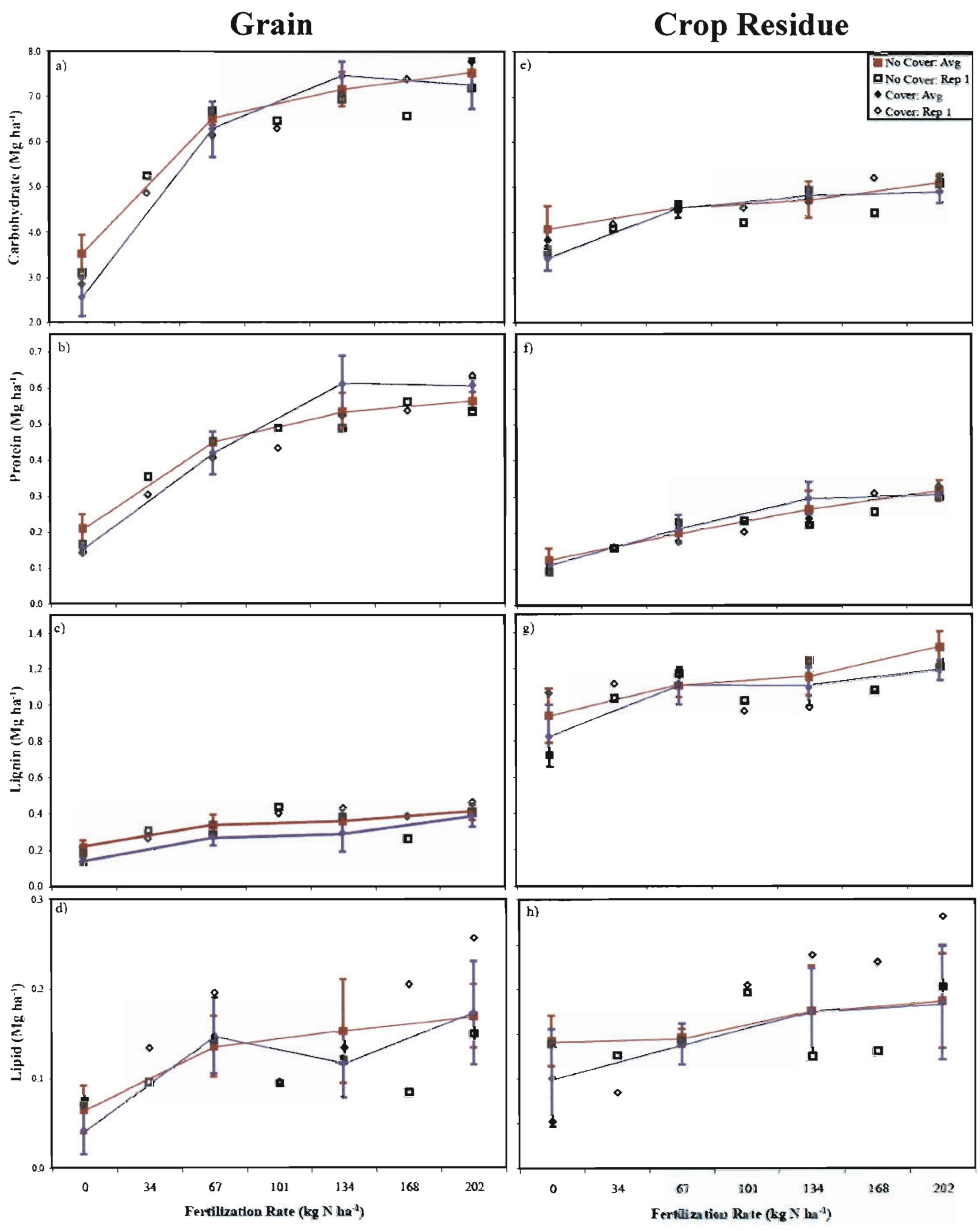

Figure 31. Biochemical Stocks of Corn Grain and Residue

Biochemical stock yields for carbohydrate, protein, lignin and lipid in the grain and crop residue over seven N fertilization rates, both with (purple and open diamonds) and without a cover crop (red and open squares). Solid red squares at 0, 67, 134, and 202 kg N ha^{-1} are average stock values for R1-R4 grown without a cover crop. Solid purple diamonds at 0, 67, 134, and 202 kg N ha^{-1} are average stock values for R1-R4 grown with a cover crop. Error bars on these points represent natural variability. Open diamonds and squares are R1 stocks for crops grown without and without a cover crop, respectively.

Costs: The Cost Assessment Model

Standard costs of crop production in the cost assessment model include: seed, herbicide, labor, machinery and fuel for planting and harvest, and transportation costs (Table 13). We estimate it costs \$558 ha^{-1} to crop for corn without fertilizer, a cover crop, or harvesting the crop residue.

<u>Cover Crop Costs</u>

Using a cover crop as a sustainable agriculture management technique has minimal impact on production cost for this field site (Table 13). The additional cost of the cover crop is from the seed (\$20.25 ha^{-1}), the labor for planting (\$2.78 ha^{-1}) and the diesel used to operate the machinery (\$3.79 ha^{-1}). There is no additional cost associated with the purchase of the herbicide, its application, or with tilling the cover crop into the soil since these processes would have been applied even if the cover crop was not used (i.e. these were all done for the no cover crop treatment). The total cost of using a cover crop was estimated as \$27 ha^{-1}. The use of a cover crop can increase yield over the long-term, and thereby increase profits, by maintaining soil organic matter and nutrient content (Snapp et al. 2005).

<u>Nitrogen Fertilization Costs</u>

Cost of N fertilization includes the cost of the actual fertilizer (\$0-\$220 ha^{-1} depending on rate) and the cost of labor (\$4.63 ha^{-1}). Though for this experiment N fertilizer was applied by hand, we also include the cost of diesel (\$7.55 ha^{-1}) for apply N fertilizer with a machine. For the unfertilized plots there is no cost for N fertilization. The average cost of ammonium nitrate fertilizer was \$366 per ton in 2006, or \$1.09 per kg N (ERS 2008; Maguire et al. 2009). Therefore, the cost of N fertilization increases linearly according to the rate applied (Table 13).

<u>Residue Harvest Costs</u>

Total cost to harvest the grain includes standard operational costs, the cost of a cover crop (if used), and the cost of the fertilization rate chosen (Table 15a). If cropping for both grain and residue, an additional cost to harvest the crop residue (\$12 ha^{-1}; Table 13) is included (Table 15b). The cost to harvest the crop residue includes labor (\$3.70 ha^{-1}) and diesel used (\$8.76 ha^{-1}). We assume there are no additional machinery costs for residue harvesting, since these costs are incurred for planting and harvesting the grain (the primary commodity).

Table 15. Total Cropping and Harvest Cost to the Farm Gate

The total cost of corn production for a) grain harvest and b) grain and residue harvest under varying agricultural management techniques (fertilization rates and use of a cover crop).

a) Total Cost to Harvest Grain Only		
Fertilization Rate ($kg\ N\ ha^{-1}$)	**Fertilizer**	**Fertilizer and Cover Crop**
0	\$558	\$585
34	\$607	\$634
67	\$643	\$670
101	\$681	\$707
134	\$717	\$743
168	\$754	\$781
202	\$791	\$818
b) Total Cost to Harvest Grain & Residue		
Fertilization Rate ($kg\ N\ ha^{-1}$)	**Fertilizer**	**Fertilizer and Cover Crop**
0	\$571	\$597
34	\$620	\$647
67	\$656	\$683
101	\$693	\$720
134	\$729	\$756
168	\$766	\$793
202	\$803	\$830

Cropping for Mass Yield

The addition of a cover crop has no significant impact on total aboveground corn plant yields (p-value =0.210), as reported in McSwiney et al. (2010). There is also no difference in corn grain yield for corn grown with a cover crop or without (McSwiney et al. 2010). Both total aboveground yield and grain yield have significant responses to N fertilization (p-value < 0.0001; McSwiney et al. 2010).

We analyzed the cost efficiency of cropping for total aboveground and grain mass yield using the data provided in McSwiney et al. (2010) and the cost assessment model. Whether cropping for total aboveground yield or for grain yield, above ~67 kg N ha^{-1}, additional spending on fertilizer has negligible impact on yields (p-values ranging from 0.055-0.919 when comparing 67 kg N ha^{-1} to either 134 or 202 kg N ha^{-1}; Fig 32a; Fig 32b). This is true whether cropping with or without a cover crop. Only when unfertilized does the use of a cover crop impact cost per yield for either total aboveground or grain mass (p-values = 0.010 and 0.025, respectively). Figs. 32c and 32d show that at 67 kg N ha^{-1}, the cost to produce 1 Mg of yield, whether total aboveground mass or grain mass, respectively, is lowest, and additional fertilizer does not improve returns.

Although grain yield slightly increased at fertilization rates above 67 kg N ha^{-1} (Fig. 32b), the financial benefit of this grain yield increase was offset by the cost associated with increased fertilizer. For this reason, Fig. 32d is flat beyond 67 kg N ha^{-1}. Were corn grain to become more valuable, it would become profitable to apply more fertilizer. Conversely, were the value of grain to drop, farmers' risk of economic loss would be increased by more fertilizer application.

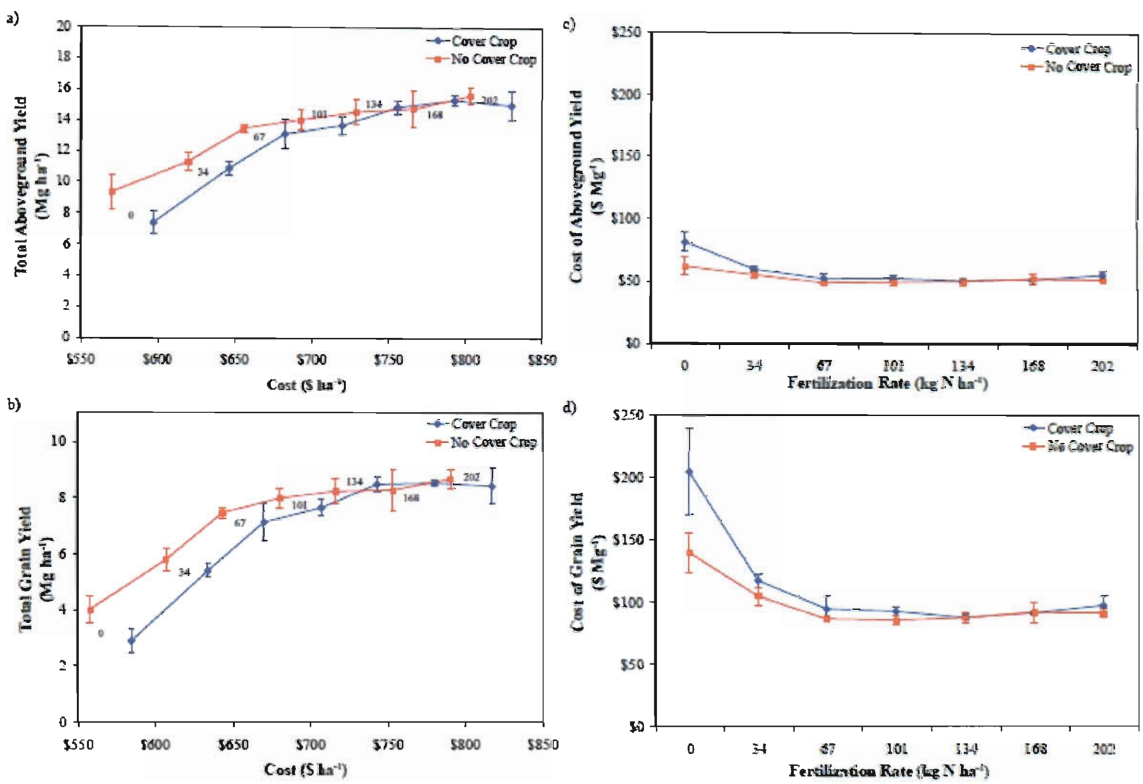

Figure 32. Cost of Cropping for Corn Mass Yield

The response of mass yield, for total aboveground (Fig. 32a) and grain (Fig. 32b), to additional monetary inputs (i.e. increasing costs to farmers). These inputs include the addition of a cover crop (blue diamonds) and increasing fertilization rates (the numbers on Figs. 32a and 32b represent the fertilization rate (kg N ha^{-1}) for the red square (no cover crop) and blue diamond (cover crop) points surrounding it). This response can also be represented as the amount of money required from the farmer to produce 1 Mg of yield (either total aboveground- Fig. 32c or grain- Fig. 32d).

Cropping for Food: Grain Protein

If the corn grain being produced is intended to be used as food, ^{13}C NMR could be used to crop specifically for that goal, focusing on maximizing corn grain protein yields. For some crops, such as wheat, cropping to maximize protein is an economic necessity since farmers receive an additional monetary premium for wheat crops with higher protein concentrations (Bale and Ryan 1977; Baker et al. 2004). Corn grain protein yields stop responding to additional inputs (i.e. N fertilizer) to the ecosystem between 67 – 134 kg N ha^{-1} (Fig. 33). Applying higher fertilization rates (e.g. 134 - 202 kg N ha^{-1}) requires additional funds but does not produce additional protein yields.

When considering cover crops, above 67 kg N ha^{-1} there is no difference in cost per protein yield when grown without a cover crop (p-values > 0.27; Fig. 33). When grown with a cover crop, fertilizing at 134 kg N ha^{-1} does produce better returns per cost than cropping at 67 kg N ha^{-1} (p-value = 0.037). It is likely that cost per protein yield is minimized between 101 – 134 kg N ha^{-1} when grown with a cover crop (Fig. 33).

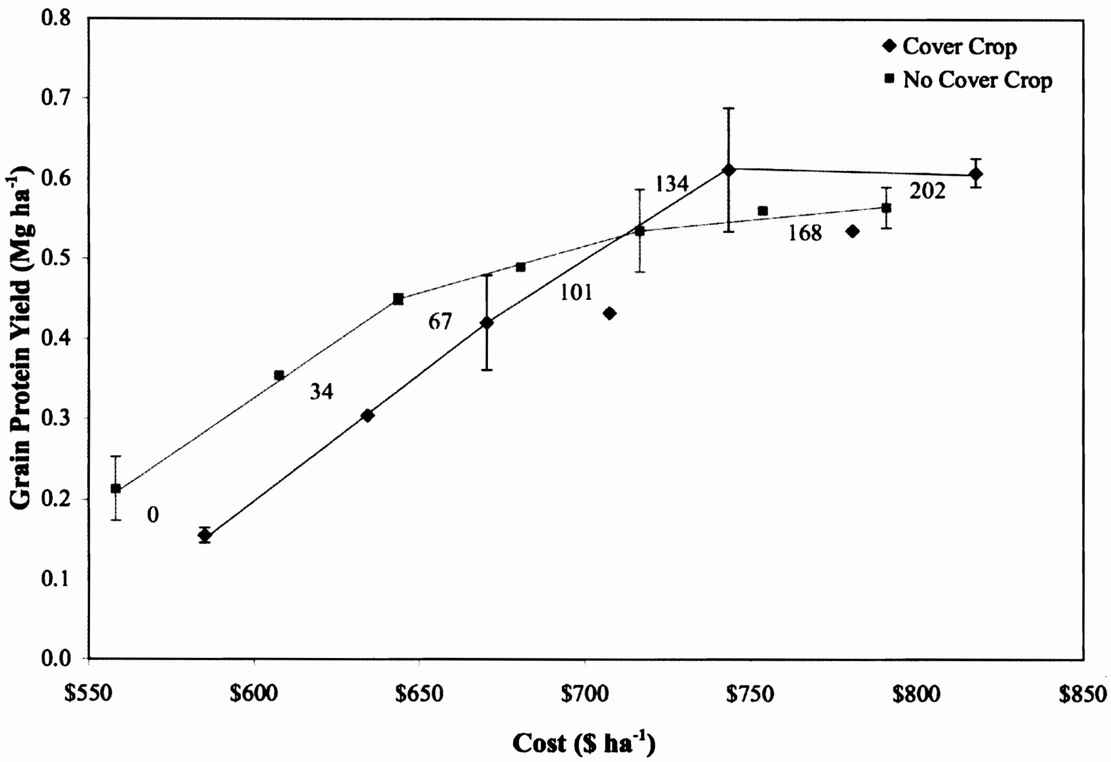

Figure 33. Cost of Cropping for Corn Grain Protein Yield

The amount of grain protein yield (Mg ha^{-1}) produced under different agricultural management techniques (blue diamond-cover crop; red square-no cover crop; values – N fertilization rates for surrounding two points). Additional monetary inputs into the corn agricultural ecosystem have diminishing returns on protein yield.

Precision Agriculture

A newer sustainable agriculture technique is precision agriculture (Gebbers and Adamchuk 2010). Broadly, precision agriculture is the use of technology (e.g. machinery, GPS, remote sensing) to implement agricultural management techniques to maximize yields by taking into account the specific crop, cropping system, and area (e.g. climatology, and soil profiles; Matson et al. 1997; Robert 2002).

In terms of N fertilization, precision agriculture gives farmers the ability to vary fertilizer rates and types within their fields to maximize yield, through monitoring changes in crop N status over space and time (Robert 2002; Boggs et al. 2003). This benefits not only the environment, but also the farmer, both financially and in time and labor. Whether a crop is to be used for food or for fuel, a fundamental concept of precision N management is that it is critical to maximize crop yield while minimizing fertilizer application and energy consumption to mitigate environmental degradation.

Many precision agriculture techniques use chemical analyses of plant organic matter (OM) to make crop management decisions. Analyses that measure or estimate biochemical composition (Wessman et al. 1988; Curran et al. 2001), N content (Curran 1989), or chlorophyll content (Jago et al. 1999) shed light on the quality of crop biomass and allow farmers to alter techniques, particularly N fertilization, to improve crop quality (Gebbers and Adamchuk 2010). Biological assays and near infrared spectroscopy (NIRS) are methods currently used for these analyses (Card et al. 1988; Curran et al. 2001). NIRS is a fast and easy technique, but must be calibrated to biological assays, which can be inaccurate. Solid-state ^{13}C nuclear magnetic resonance spectroscopy can also be used to estimate crop quality (Gallagher et al. In Review), and could eventually be used to improve NIRS calibrations.

Solid-state ^{13}C NMR, coupled with a molecular mixing model (Baldock et al. 2004), measures crop biochemistry (carbohydrate, protein, lignin, lipid) and is sensitive enough to detect changes in plant biochemical composition over a N gradient (Gallagher et al. In Review). This method has the potential to improve precision agriculture techniques in two ways: 1) through more accurate calibrations of remote sensing precision agriculture techniques and 2) by allowing farmers to shift from cropping for total mass yield to cropping for total yield of a specific biochemical, which is the focus of this paper.

Analyzing crops using ^{13}C NMR has the potential to take precision agriculture further by allowing farmers to maximize for a targeted biochemical (e.g. carbohydrates for cellulosic ethanol, or protein for food) or a biochemical profile (high carbohydrate, low lignin concentrations for efficient conversion into cellulosic ethanol), making precision N management of particular relevance to the biofuel industry. The biofuel industry relies on agriculture for its feedstocks, whether corn grain for grain ethanol or crop residues (e.g. corn stover, wheat straw) and dedicated grassland crops (e.g. switchgrass) for cellulosic ethanol (McKendry 2002). To ensure long-term viability of the biofuel industry, sustainable agricultural practices need to be used to maintain a stable feedstock supply with time and minimize the industry's environmental impacts (Robertson et al. 2008).

Whether sustainable agriculture techniques are implemented or not is, in part, dependent on their benefits and short-term cost-efficiency. Fertilization is an economic trade-off: it increases yield at the expense of increased costs and environmental impacts. If a particular biochemical (e.g. carbohydrate) is not responsive to fertilization, there will be a threshold beyond which fertilization is no longer cost-effective. The lack of a financial incentive, coupled with negative environmental impacts, creates a strong argument against excessive fertilizer use.

We begin with a biochemical stocks study using ^{13}C NMR, which is a first step in improving precision agriculture through the calibration of a cheap, and fast precision agriculture technique, near infrared spectroscopy (NIRS). Here we analyze the cost-efficiency of cropping for a targeted biochemical (carbohydrate), while varying agricultural management techniques (N fertilization rate, and the use of a cover crop). We measure biochemical stocks (carbohydrate, protein, lignin, and lipid) for corn grain and corn crop residue, the two commodities in a corn agricultural ecosystem. To understand the economic implications of growing crops not just for mass yield, but specifically for carbohydrate yield, we developed a simple cost assessment model based on Pimentel et al. (2009). Using this model we compare the cost-effectiveness of growing grain for food or fuel and harvesting crop residue for cellulosic ethanol.

Site Description

The N rate experiment is located at the W.K. Kellogg Biological Station –Long Term Ecological Research (KBS-LTER) Main Site (42° 24'N, 85° 24'W) in southwest Michigan, USA. The KBS-LTER received 102.9 cm of precipitation and its average temperature was 11.7 °C during 2006 (KBS-LTER 2009). Further information about the KBS-LTER sites can be found at http://lter.kbs.msu.edu.

Seven different N fertilization rates of 28% urea ammonium nitrate (0, 34, 67, 101, 134, 168, and 202 kg N ka^{-1}) were applied to a corn monoculture ecosystem replicated in four (McSwiney et al. 2010). All of the replicates were split into halves; one half was planted with a winter wheat cover crop and the other without (Fig. 29). The cover crop was used to prevent soil erosion and nutrient leaching during winter months (McSwiney et al. 2010). Before the corn was planted in the spring, herbicide was applied to all treatments (cover and no cover), killing the winter wheat (and any weeds present), which was then tilled into the soil. Here we present results for replicates R1-R4 for both the cover crop and no cover crop treatments at fertilization rates 0, 67, 134, and 202 kg N ha^{-1}. Samples from the cover crop and no cover crop R1 treatment grown under 34, 101, and 168 kg N ha^{-1} were also analyzed. Samples were split according to plant organ: grain, leaf and stem, and reproductive support (husk, shank, tassel, and cob). The combination of leaf and stem and the reproductive support makes up the corn plant residue that remains after harvest (from now on referred to as crop residue). Further details on the processing and sampling can be found in McSwiney et al. (2010).

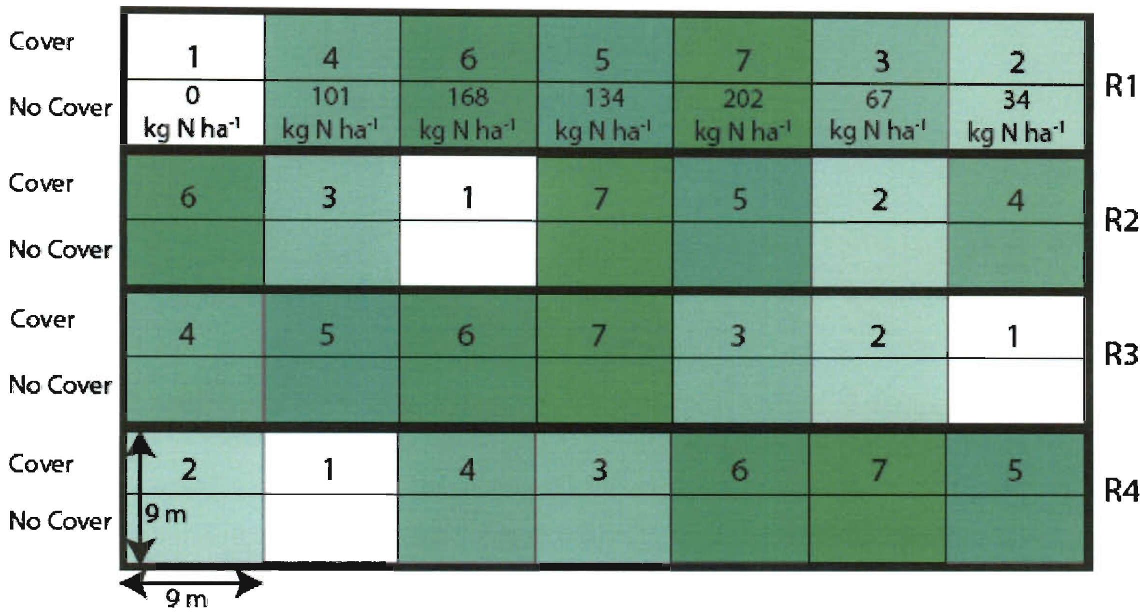

Figure 29. Nitrogen Rate Experiment

The N fertilization experiment consists of seven N fertilization treatments replicated in four and split into a winter wheat (cover) and no winter wheat cover crop (no cover). Here we present results from replicate 1 for both no cover crop and cover crop treatments over the seven fertilization rates (0, 34, 67, 101, 134, 168 and 202 kg N ha^{-1}) and replicates 2, 3, and 4 for four of the seven fertilization rates (0, 67, 134, 202 kg N ha^{-1}).

Methods

We assess plant biochemistry (carbohydrate, protein, lignin, and lipid concentrations) using a ^{13}C NMR (Baldock et al. 2004; Nelson and Baldock 2005). NMR is a more accurate technique for characterizing OM biochemistry than biological assays since it is nondestructive and is able to quantify organic functional groups present in plant biochemicals without chemical pretreatment or extraction (Nelson and Baldock 2005). Biological assays are usually compound-specific, often extract compounds unrelated to the target compound, and detects between 20-80% of C present in a sample (Harmon and Lajtha 1999).

We measured C and N concentrations using Costech 4010 and Perkin-Elmer 2400 Series CHNS/O Elemental Analysis systems (Appendix A3). Solid-state ^{13}C NMR was performed on a Bruker 200 MHz NMR. We performed cross polarization (CP) experiments using a 4mm magic angle spinning (MAS) probe, 5 kHz MAS frequency, 1 ms contact time and a recycle delay >2 sec on one replicate of each plant organ under all fertilization rates (Appendix D2). For fertilization rates 0, 67, 134, and 202 kg N ha^{-1}, CP experiments were performed on all four replicates to analyze for natural variability. All spectra were corrected for spinning side bands (SSB) and spin-counted (Smernik and Oades 2001), with an average of 77.7±6.8% of C detected. No spectra detected less than 64.6% of the sample C. All underdetection of C is accounted for in mobile C molecules (i.e. lipids; Gallagher et al. In Review). A molecular mixing model (MMM) was used to determine the biochemical composition (Appendix B2) of each corn biomass sample based on the acquired ^{13}C NMR spectra and the measured C and N content (Baldock et al. 2004).

^{13}C Nuclear Magnetic Resonance Spectroscopy and the Molecular Mixing Model

The MMM uses a sample's C:N ratio and six predefined ^{13}C NMR spectral regions to break a sample's NMR spectra into four biochemical classes (carbohydrate, lignin, lipid, and protein) and then calculates the percentage of each biochemical in the sample using spectra from standards that are representative for each class (e.g. cellulose for carbohydrate). Carbon-13 NMR experiments conducted in our lab using known mixtures of purified biopolymers indicate that the MMM deconvolutes NMR spectra into four main biochemical classes with an accuracy of ±1.0% (Gallagher et al. In Review).

Cost Assessment Model

We developed a simple cost assessment model (Table 13) based on the work of Pimentel et al. (2009) to explore the cost-effectiveness of cropping grain for food or fuel under varying sustainable agriculture techniques. Cost-effectiveness refers to farmers receiving the maximum amount of yield per cost invested into the crop ecosystem in one year (in other words, the minimum amount of cost to produce 1 Mg of yield). We estimate the cost to produce one Mg of mass yield for total aboveground biomass (grain and residue) and for grain yield. We also calculate the cost to produce one Mg of carbohydrate yield per hectare for grain for corn grain ethanol and residue for cellulosic ethanol production. In addition, we analyze the relationship of cost to corn grain protein yield. We modeled cost according to the method of Pimentel et al. (2009), adjusted to our experiments' specific agricultural conditions (Table 13; Fig. 30). Table 13 shows all the parameters used in our cost assessment to calculate: 1) standard agricultural operational costs (i.e. planting and grain harvest costs), 2) cost of the cover crop, 3) cost of the application of fertilizer, and 4) the cost to harvest the crop residue. Using Eqn. 20

and these parameters, we calculate the total cost for different agricultural scenarios, where fertilizer, cover crop, and residue harvest costs vary based on use (Fig. 30).

$$\text{Total Cost} = \text{Standard Operation Cost (+Fertilizer Cost) (+Cover Crop Cost) (+Residue Harvest Cost)} \quad \text{Eqn. 20}$$

Combining the results from Eqn. 20 with total aboveground, grain, carbohydrate, and protein yield data (for both the grain and crop residue; Table 14), we were able to estimate the cost per yield using Eqn. 21:

$$\text{Cost per Yield (\$ Mg}^{-1}\text{)} = \frac{\text{Total Cost (\$ ha}^{-1}\text{)}}{\text{Yield (Mg ha}^{-1}\text{)}} \quad \text{Eqn. 21}$$

We do not include the cost of environmental impacts in our estimations of the total cost to grow the corn crop (Eqn. 20). Estimating environmental costs requires converting environmental consequences (e.g. land use change, greenhouse gas emissions, etc.) into monetary units, which can have impacts on different timescales (e.g. Hill et al. 2009), and is beyond the scope of this work. Therefore, our results should be considered lower bounds on the total cost of corn agricultural production.

Statistical Analysis

Statistical significance was determined using a two-tailed t-test (paired, two-sampled, unequal variance). A significance level, α, of 0.05 was used for all comparisons, indicating that p-values below this level were significant (i.e. p-values $\leq$ 0.05 imply that there is $\leq$ 5% chance of erroneously reporting differences between experimental treatments, a Type I error). T-tests were used to compare cost per yield for total mass, grain mass, grain protein, grain carbohydrate and residue carbohydrate under different N fertilizer rates and cover crop treatments (Appendix C5).

Table 13. Cost Assessment Model

A simple cost assessment model adapted from Pimentel et al. (2009). All parameter values are for the planting-harvest season 2005-2006, when the N Rate Experiment took place. Though the N fertilizer for this experiment was applied by hand, we include a cost for the amount of diesel that would have been consumed if the fertilizer had been applied by machine (West and Marland 2002). We assume that when harvesting the crop residue there are no additional costs for machinery other than those occurred with standard operational costs, only the cost of operating the machinery (i.e. diesel). We round costs to the nearest dollar per hectare.

Notes:

[a] Estimated time (hrs ha^{-1}) to: fertilize with potash, chisel plow, finish, plant, cultivate and harvest (McSwiney unpublished data)

[b] Field worker average wage (\$ hr^{-1}) for 2006 (NASS 2006a)

[c] Estimated machinery cost (\$ ha^{-1}) (Pimentel et al. 2009)

[d] Estimated amount of diesel required (L ha^{-1}); includes diesel for moldboard plow, disk, planting, single cultivation, pesticide application, and harvest with combine (West and Marland 2002)

[e] Price of diesel (\$ ha^{-1}) in 2006 (EIA 2009); conversion factor: 1 L = 0.2641 gallons

[f] 81,543 corn seeds planted per hectare (McSwiney et al. 2010); a higher seeding rate than the "usual practice" of ~ 70,000 seeds ha^{-1} (http://lter.kbs.msu.edu/datatables/21)

[g] April 2006 corn seed price (\$ bu^{-1}) from the National Agriculture Statistics Service May 2006 report (NASS 2006b)

[h] Conversion: assuming average of 90,000 kernels per bushel (Lee and Herbek 2005)

[i] Amount of herbicide applied (kg ha^{-1}) (kg of active ingredient- glyphosate) (McSwiney et al. 2010)

[j] Cost of glyphosate herbicide (\$ ha^{-1}) in 2006 (NASS 2006c); assuming herbicide formulation: 360 g L^{-1} and conversion: 3.7836 L per gallon

[k] Cost of transportation (\$ ha^{-1}) of machinery, fuel, & seed for production (Pimentel et al. 2009)

[l] Estimated time to plant (hrs ha^{-1}) (McSwiney unpublished data)

[m] Estimated amount of diesel required for planting (L ha^{-1}) (West and Marland 2002)

[n] Amount of winter wheat seed planted (kg ha^{-1}) (McSwiney et al. 2010)

[o] September 2005 winter wheat seed price (\$ bu^{-1}) (from NASS Oct. 2005 report) (NASS 2005b)

[p] Conversion: 1 bushel wheat = 60 lbs wheat; 1 lb = 0.4536 kg

[q] Estimated time to apply starter N fertilizer and the N fertilizer differentiate (hrs ha^{-1}) (McSwiney unpublished data)

[r] Estimated amount of diesel required to for fertilizer application (L ha^{-1}) (West and Marland 2002)

[s] Average cost of ammonium nitrate fertilizer (\$ ton^{-1}) in 2006 (ERS 2008)

[t] Assuming ammonium nitrate fertilizer is 33% N by weight; conversion: 1 ton = 1016.064 kg (Maguire et al. 2009)

[u] Estimated time to harvest (hrs ha^{-1}) (McSwiney unpublished data)

[v] Estimated amount of diesel required to harvest with a combine (L ha^{-1}) (West and Marland 2002)

Table 13. Cost Assessment Model (cont.)

STANDARD OPERATIONAL COSTS				
		Quantity	**Rate**	**Cost ($ ha^{-1})**
Labor		2 hrs ha^{-1} [a]	$9.25 hr^{-1} [b]	$18.50
Machinery		~	~	$310.00 [c]
Diesel		49.03 L ha^{-1} [d]	$2.91 gal^{-1} [e]	$37.68
Corn Seed		81,543 seed ha^{-1} [f]	$2.11 bu^{-1} [g]	$1.91 [h]
Herbicide		0.46 kg ha^{-1} [i]	$29.30 gal^{-1} [j]	$10.10
Transportation		~	~	$180.00 [k]
TOTAL				$558
COVER CROP COSTS				
		Quantity	**Rate**	**Cost ($ ha^{-1})**
Labor		0.3 hrs ha^{-1} [l]	$9.25 hr^{-1} [b]	$2.78
Diesel		4.93 L ha^{-1} [m]	$2.91 gal^{-1} [e]	$3.79
Winter Wheat Seed		168 kg ha^{-1} [n]	$3.28 bu^{-1} [o]	$20.25 [p]
TOTAL				$27
FERTILIZER COSTS				
	Fertilizer Rate (kg N ha^{-1})	**Quantity**	**Rate**	**Cost ($ ha^{-1})**
Labor	~	0.5 hrs ha^{-1} [q]	$9.25 hr^{-1} [b]	$4.63
Diesel	~	9.82 L ha^{-1} [r]	$2.91 gal^{-1} [e]	$7.55
Fertilizer	0	~	$366 ton^{-1} [s]	$0.00 [t]
	34	~	$366 ton^{-1} [s]	$37.11 [t]
	67	~	$366 ton^{-1} [s]	$73.13 [t]
	101	~	$366 ton^{-1} [s]	$110.25 [t]
	134	~	$366 ton^{-1} [s]	$146.27 [t]
	168	~	$366 ton^{-1} [s]	$183.38 [t]
	202	~	$366 ton^{-1} [s]	$220.49 [t]
TOTAL	0			$0
	34			$49
	67			$85
	101			$122
	134			$158
	168			$196
	202			$233
CROP RESIDUE HARVEST COSTS				
		Quantity	**Rate**	**Cost ($ ha^{-1})**
Labor		0.4 hrs ha^{-1} [u]	$9.25 hr^{-1} [b]	$3.70
Diesel		11.4 L ha^{-1} [v]	$2.91 gal^{-1} [e]	$8.76
TOTAL				$12

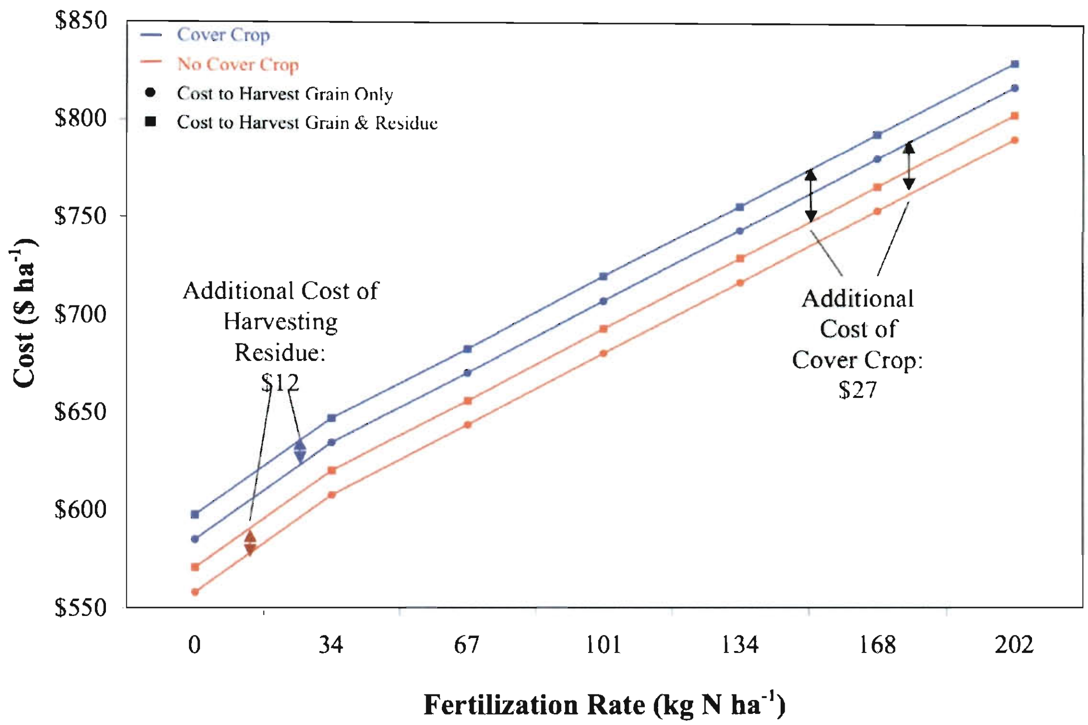

Figure 30. Total Cost to Grow and Harvest Corn Crop

The total cost produce a corn crop and harvest its grain or both its grain and residue. The largest component of corn agricultural costs are the standard operating costs (\$558 ha^{-1}), which include machinery, labor and materials to prep fields, planting, maintain fields, grain harvesting, corn seed, diesel and transportation (machinery, seeds, fuel) costs. The application of N fertilizer can increase these costs by up to \$233 ha^{-1} depending on rate. The additional costs to apply a cover crop (\$12 ha^{-1}) and harvest the residue (\$27 ha^{-1}) are minimal by comparison. These costs do not account for environment costs.

Cropping for Fuel: Carbohydrate

If a corn crop ecosystem is grown for biofuels, using ^{13}C NMR data can help farmers select management techniques to maximize the biochemical yield or biochemical profile of the crop for specific industrial uses. A corn crop can be used as a feedstock for several biofuels: 1) corn crop residue for bio-oil (produced from pyrolysis), 2) corn grain for corn grain ethanol, and 3) corn crop residue for cellulosic ethanol. For corn grain ethanol production, carbohydrate, in particular starch, is the biochemical converted into ethanol for fuel (Sanchez and Cardona 2008). For cellulosic ethanol production, carbohydrate is also the biochemical class used for conversion, primarily in the form of cellulose (Sanchez and Cardona 2008). Lignin hinders the conversion of carbohydrates into simple sugars, since it is difficult for enzymes to degrade (Hamelinck et al. 2005). This is a bigger concern in the cellulosic ethanol industry than in the grain ethanol industry, since feedstocks for cellulosic ethanol typically have high lignin concentrations (Fig. 31g) (McKendry 2002). Corn grain has low concentrations of lignin (Fig. 31c), particularly in relation to carbohydrate concentrations (McKendry 2002) (carbohydrate:lignin ratio of 16-20 depending on fertilization rate, versus crop residue carbohydrate:lignin ratios of 3-5). Since lignin concentrations increase with increasing fertilization (Gallagher et al. In Review), it is critical to maximize residue carbohydrate yields at lower fertilization rates in order to minimize lignin yields.

<u>Grain</u>

If a corn grain crop is to be produced for grain ethanol production, agriculture management techniques should be chosen to maximize carbohydrate yield. At 134 kg N ha^{-1}, there is no additional gain in grain carbohydrate yield with additional monetary inputs, primarily through N fertilizer (Fig. 34a). The cost to produce 1 Mg of grain carbohydrate is minimized at this fertilization rate (Fig. 34b). However, between the 67 to 202 kg N ha^{-1} there is little difference in the cost per yield produced (Fig. 34b). There is no statistical difference in cost per carbohydrate yield produced between 67 and 134 kg N ha^{-1}, whether grown with or without a cover crop (p-values=0.260 and 0.620, respectively.

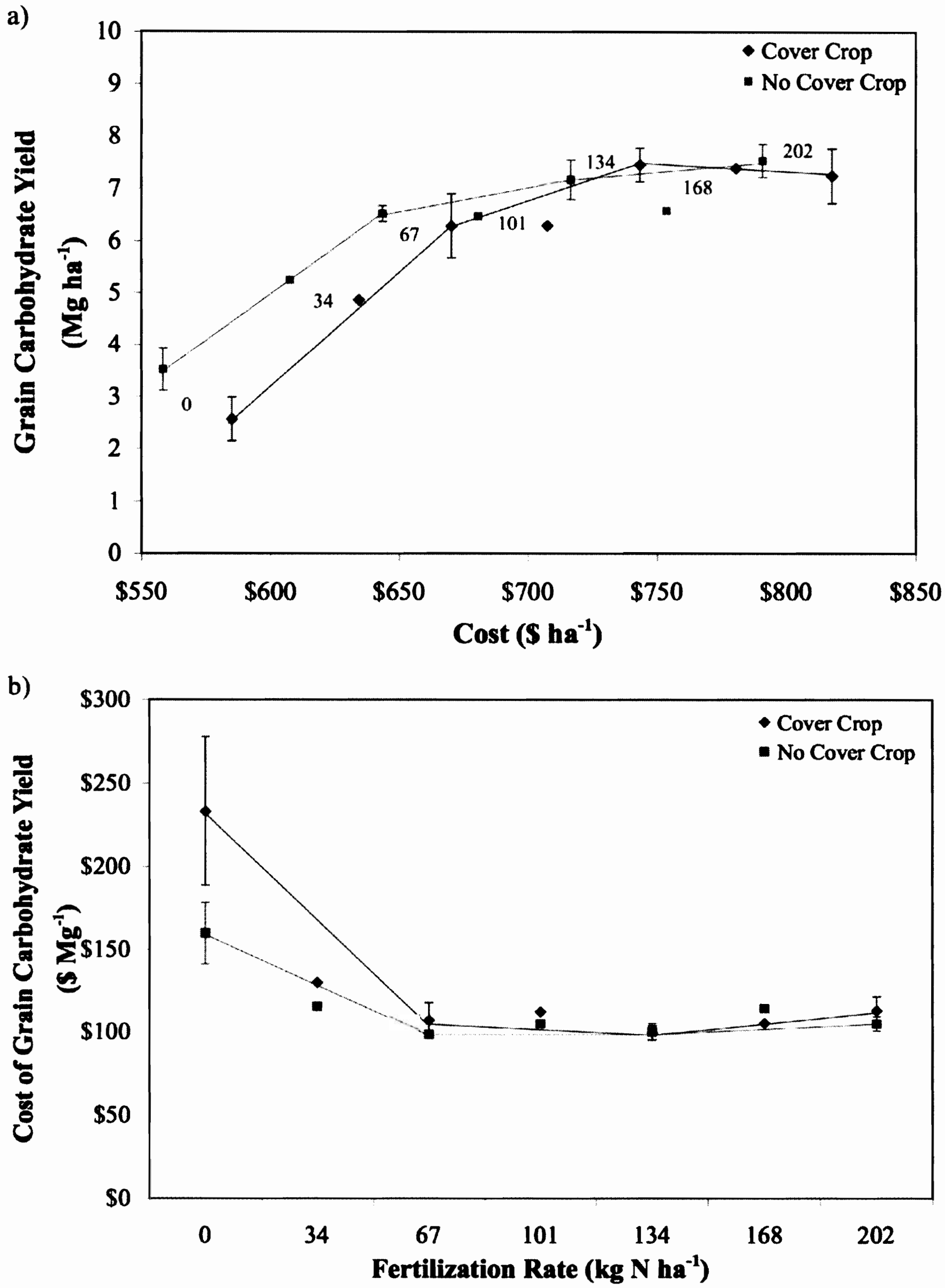

Figure 34. Cost of Cropping for Corn Grain Carbohydrate Yield

The response of grain carbohydrate yield (Mg ha^{-1}) to additional monetary inputs (Fig 34a). These inputs include the addition of a cover crop (blue diamonds) and increasing fertilization rates (the numbers represent the fertilization rate (kg N ha^{-1}) for the red square (no cover crop) and blue diamond (cover crop) points surrounding it). This response can also be represented as the amount of money required from the farmer to produce 1 Mg of grain carbohydrate yield (Fig 34b).

Residue

All the cost of corn production is for grain yield production. Corn crop residue is a secondary product of corn agriculture and therefore the only cost associated with cropping for residue is the cost of harvesting the residue. Altering sustainable management techniques (e.g. using a cover crop; varying fertilization rates) has no impact on this cost. The cost of cropping for residue carbohydrate is lowest at 202 kg N ha^{-1}. However, there is little difference between costs per carbohydrate yield above 67 kg N ha^{-1}. Cropping at 67 kg N ha^{-1} is the same as cropping at 134 kg N ha^{-1}, whether grown with or without a cover crop (p-values=0.055 and 0.450, respectively. Cropping at 67 kg N ha^{-1} costs \$2.8 per carbohydrate yield, while cropping at 202 kg N ha^{-1} costs between \$2.4-\$2.5 per carbohydrate yield (depending on cover crop). Though cropping at 67 kg N ha^{-1} costs more than at 202 kg N ha^{-1} (p-values=0.055 and 0.002), when environmental impacts are considered, it is unlikely that a reduction of \$0.40 Mg^{-1} will be worthwhile. Most likely there is no difference in cost per yield between 34 – 67 kg N ha^{-1} (Fig. 35), but since we do not have replicated data for 34 kg N ha^{-1}, we cannot say this with any statistical confidence.

Whether a farmer will harvest their crop residue to sell as a cellulosic ethanol feedstock will depend on the price being paid. This price needs to outweigh both the cost of harvest (\$12 ha^{-1}) and the additional environmental costs (e.g. soil erosion, reduced SOM and soil nutrients), as well as impacts on future crop yields before it becomes cost-effective to harvest for crop residue.

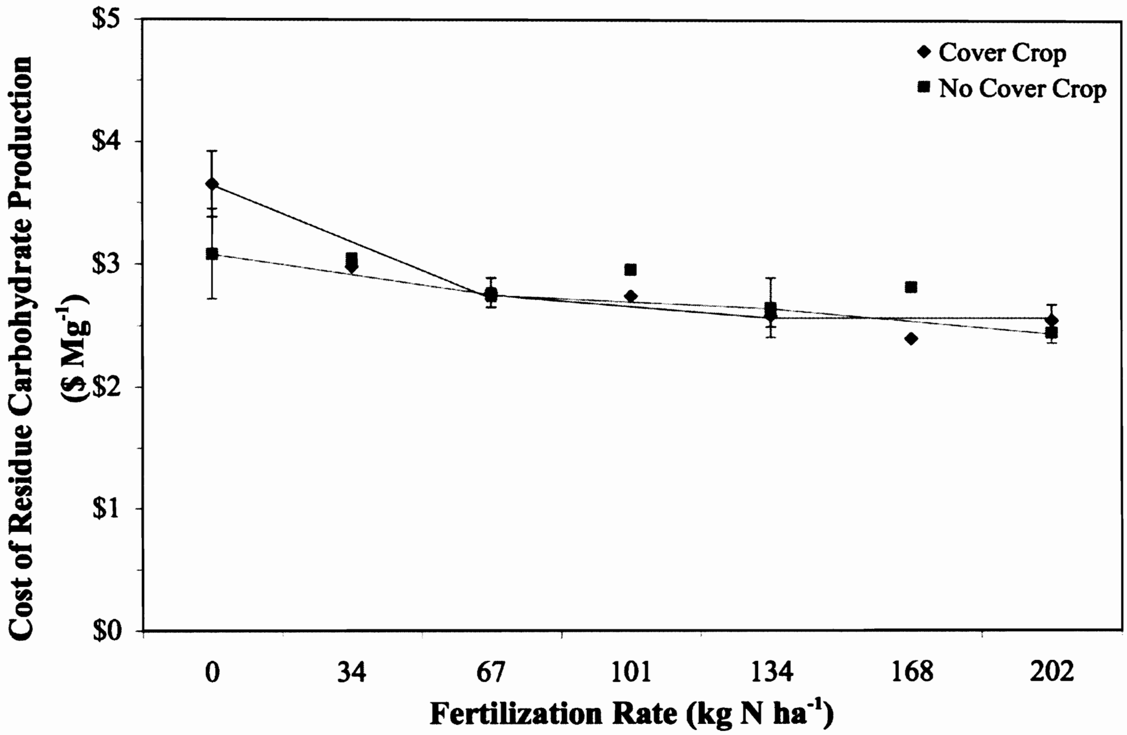

Figure 35. Cost of Cropping for Corn Residue Carbohydrate Yield

The cost of producing 1 Mg of residue carbohydrate yield (\$ Mg^{-1}) for corn grown under different agricultural management techniques (blue diamond-cover crop; red square-no cover crop; values – N fertilization rates for surrounding two points).

C-13 NMR as a Precision Agriculture Tool

C-13 NMR could be a beneficial precision agriculture tool in two ways, 1) by allowing farmers to adjust sustainable agricultural management techniques to crop for specific biochemicals (protein-food, carbohydrate-biofuel), and 2) by improving the calibration and verification of other precision agriculture techniques that use remote sensing.

From the N rate experiment data reported here, it is clear that ^{13}C NMR will allow farmers to select management techniques, such as N fertilization rate, to maximize for a specific biochemical. The benefit of this becomes even more apparent when you consider the fact that the majority of farms operate on a much larger scale than described here. The N rate experiment's individual plots were 4.5 by 9 m in size (40.5 m^2 = 0.004 ha = 0.01 acres). The total experimental area was ~ 2300 m^2, a little over half an acre (0.5 acres). The average farm size in the U.S. is 418 acres, with only 11% of farms less than 10 acres in size (NASS 2007a). For the major U.S. crops, corn, soybean, and wheat, average farm sizes are even larger at 745 acres, 731 acres, and 1,468 acres, respectively (NASS 2007a). On these larger scales, farmers can have more variability in mass yield and biochemical returns due to spatial variations in soil properties, water supply, etc. C-13 NMR may be able to detect these spatial variations and allow farmers to adjust their management techniques accordingly.

In addition to cropping for biochemicals, ^{13}C NMR can also improve remote sensing precision agriculture techniques through better calibration and verification. Remote sensing has become a useful technique in precision N management. Plant biochemical concentrations have been estimated for decades in laboratories using methods based on surface reflectance and radiative properties. Recently these techniques have been modified for use at the canopy scale using airborne and spaceborne remote sensing detectors (Curran 1989). Such modifications have made possible the transition from observing properties of a single leaf in the lab (e.g. using NIRS), to observing leaves and plants in the field (e.g. using portable radiometers), to regional and global scale observations of plant biochemistry (e.g. using AVIRIS –airborne visible/infrared spectrometer and Landsat and Hyperion satellites).

NIRS has been used to estimate concentrations of chlorophyll (a, b, total), starch, sugars, cellulose, lignin, proteins, amino acids, water, total N, and phosphorus in plant samples (Card et al. 1988; Curran et al. 1992; 2001; LaCapra et al. 1996; O'Neill et al. 2002; Peterson et al. 1988). Airborne and spaceborne observations have been used with some success to measure chlorophyll, N, and lignin concentrations (Oppelt and Mauser 2004; Serrano et al. 2002). Several studies have shown strong correlations between AVIRIS spectral regions and AVIRIS-based N content estimates with measured N content of plants (Asner and Vitousek 2005; Smith et al. 2002; Smith et al. 2003; LaCapra et al. 1996; e.g. Johnson et al. 1994). Gao and Goetz (1995) and Martin and Aber (1997) observed a relationship between lignin values from biological assays and the 1720 nm band in AVIRIS images of the Harvard Forest in Massachusetts. Smith et al. (2003) also found correlations between measured N content and N content estimated from Hyperion satellite reflectance data. However, accuracy of estimations of plant biochemical concentrations using spectroscopy, whether in the lab using NIRS, from the air using AVIRIS, or from space using Hyperion, is typically constrained using biological assays.

Biological assays have several disadvantages. The majority of biological assays can only estimate one compound's concentration. Since they are typically compound specific, analyzing a sample for many different types of compounds requires more biomass and can be time-consuming. In addition, biological assays chemically alter the biomass sample being analyzed (Curran 1989). It is difficult to know if the compound of interest is also being altered or how much of it is lost during the treatment. In the case of lignin, which cannot be manufactured in the laboratory, biological assays are used to generate standards. This makes independent quantification of biological assay results impossible. Some of these studies use biological assays in conjunction with spectroscopy as the measured results to compare with the NIRS-predicted results (Curran et al. 2001). This comparison does not use independent methods, making it difficult to evaluate the significance of their results. Baldock et al. (2004) reported that frequently biological assays extract anywhere from 20-80% of the biochemicals desired. Because of these problems, biological assays are not ideal; an alternative is ^{13}C NMR.

Using ^{13}C NMR for calibration and verification of laboratory and remotely sensed estimates of plant biochemical concentrations has several benefits over using biological assays. First, it is less expensive than performing biological assays. Performing multiple biological assays requires purchasing several chemicals, laboratory equipment, and at times instrument time. Second, ^{13}C NMR requires less biomass and is non-destructive, meaning any material analyzed using ^{13}C NMR can be used later in another analysis. Third, biological assays require relatively large quantities of biomass, which are then degraded and cannot be reused. In addition, ^{13}C NMR can produce a high quality spectrum in an hour without continuous instrument monitoring, while biological assays can often take days (especially if incubations, drying, or ashing is needed), and can be labor-intensive. Fourth, ^{13}C NMR is an independent method for assessing plant biochemistry. It does not use reflectance spectra to estimate biochemical concentrations, unlike some commonly used biological assays (e.g. protein; Curran et al. 2001). Finally, ^{13}C NMR is a more quantitative method than biological assays. Loss or degradation occurring during biological assays is difficult to measure because biochemical standards are sometimes generated via the same biological assay, making their measurement yield 100% by circular definition. Sample quantitation via ^{13}C NMR does not suffer from these problems.

In the future we anticipate that calibration of NIRS to ^{13}C NMR will be beneficial to agriculture. Though NIRS lacks high resolution, it is a rapid, inexpensive, sensitive, and quantitative method (Labbe et al. 2008) that, when coupled with NMR, will be able to detect crop biochemical compositional changes. Calibrating NIRS against NMR measurements will allow for the determination of crop biochemical composition in the field, rather than collecting samples to return to the lab. This will allow more freedom to collect data at multiple times during plant growth or at multiple harvest times for crops that can be harvested more than once a year (e.g. switchgrass). Since NIRS is a rapid technique it will be possible to analyze large numbers of samples in a field quickly, which will create statistically robust biochemical datasets.

Conclusions

Biochemical yields and cost-efficiency are controlled by N fertilizer rate. The most cost-efficiency fertilizer rate depends on what a farmer chooses to crop for (mass yield, grain protein or carbohydrate, or residue carbohydrate; Table 16). A typical N fertilization rate used in the Midwest is 124 kg N ha^{-1} (Grandy et al. 2006; Grandy and Robertson 2007). Traditional cropping for mass yield suggests that when harvesting grain only, 67 to 134 kg N ha^{-1} maximizes cost efficiency. If harvesting the whole plant, cost per yield is lowest when fertilized at 67 kg N ha^{-1}. Cropping for specific biochemicals can help improve crop production quantity and quality. Cropping grain for food (protein) is most cost effective between 101-134 kg N ha^{-1}, while cropping grain for fuel (carbohydrate) is most cost-effective at ~134 kg N ha^{-1}. There are no significant differences in biochemical yields or cost-efficiency with the addition of a cover crop except when unfertilized. Since the addition of a cover crop only affects biochemical yields when the ecosystem is unfertilized (and it is highly unlikely a corn ecosystem will receive no external N), and cover crops have many long-term environmental and economical benefits, we recommend the use of a cover crop.

Table 16. Recommended Fertilization Rates

Recommended N fertilization rates depending on harvest type and purpose, based upon biochemical yields and cost analysis. Recommended N fertilization rates are those that produce the highest yield in the desired biochemical, while minimizing costs. When cropping for crop residue, we recommend a fertilization rate that has a slightly higher cost per yield than higher fertilization rates, since the difference in cost per yield is small and the lower fertilization rate will have less environmental impacts

	Harvest Purpose			
Harvest Type	**Food** (Protein)		**Fuel** (Carbohydrate)	
	Cover	*No Cover*	*Cover*	*No Cover*
Grain	101-134 kg N ha^{-1}	67 kg N ha^{-1}	67 kg N ha^{-1}	67 kg N ha^{-1}
Crop Residue	X	X	34-67 kg N ha^{-1}	34-67 kg N ha^{-1}

CHAPTER 5

Conclusion

Agricultural ecosystems and their management manipulate the carbon (C) and nitrogen (N) cycles to increase crop productivity. These manipulations and interactions between agriculture and the C and N cycles have impacts on food and energy security, and on climate change. To understand these effects, the C and N cycles need to be studied using a coupled biogeochemical approach.

Solid-State ^{13}C Nuclear Magnetic Resonance Spectroscopy

I used a robust technique, solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR), to study the interaction between agriculture and the C and N cycles. Solid-state ^{13}C NMR is both qualitative and quantitative, able to measure C bonding environments without degradation to samples. Using ^{13}C NMR coupled with a molecular mixing model (MMM) developed by Baldock et al. (2004), I was able to precisely and accurately measure plant biochemical composition to within ±1%. In addition, using this technique I was able to apply a novel biochemical stocks approach to understanding how different sustainable management techniques (i.e. N fertilization and cover crop use) affect crop productivity. NMR has further implication in agriculture through precision management. Using NMR to estimate crop biochemical stocks across a field will allow farmers to alter agricultural techniques (e.g. fertilizer rate) to maximize crop yield considering temporal and spatial variations. In addition, the use of NMR to calibrate precision agriculture techniques that use remote sensing to estimate crop quality will also improve results over currently used biological assays.

The MMM is also one of several techniques developed to estimate biomass carbon oxidation state (C_{ox}). C_{ox} describes the bonding environment of C in biomass and is a critical parameter in estimating the oxidative ratio (OR) of mechanisms controlling C cycle gas exchange fluxes between the terrestrial biosphere and atmosphere. This technique for measuring OR, when compared with previous measurements via gas exchange studies, has reduced measurement uncertainty by an order of magnitude.

Ecosystem Oxidative Ratio

Oxidative ratio describes fluxes of atmospheric oxygen (O_2) and carbon dioxide (CO_2) between the terrestrial biosphere due to processes such as photosynthesis, respiration, decomposition, and fire. To know where anthropogenic CO_2 is going in the C cycle (i.e. into the atmosphere, terrestrial biosphere, or ocean C reservoirs), this parameter needs to be well constrained. I show that for agriculture, OR can vary depending on crop type (soybean – 1.112 ± 0.003, wheat – 1.035 ± 0.001, corn – 1.030 ± 0.002). I used this data to make a simple, preliminary estimate of agricultural OR for the United States of 1.060. In addition, I calculated how shifts in agriculture acreage (i.e. land use change) have altered ecosystem OR, shifting from 1.040 in 1930 to 1.060 in 2010.

I also studied the effect of N fertilizer and cover crop use on corn photosynthetic OR, both of which had no detectable effect. Another component to understanding gas exchanges between the terrestrial biosphere and atmosphere is to understand the OR associated with the decomposition flux. I performed a litterbag experiment to determine if photosynthesis and decomposition have different OR values for a corn ecosystem and observed no statistically significant difference (1.035 ± 0.003 and 1.028 ± 0.053, respectively). It should be noted that the high error associated with the respiration OR is likely due to the litterbag technique and is the reason there is no difference between the values. The OR of bulk soil organic matter (SOM), material remaining after decomposition is different from corn photosynthetic OR (1.030 ± 0.002). This difference is likely due to two factors: 1) OR associated with the SOM remaining from the previous ecosystem (forest), and 2) OR fractionation during decomposition.

Biochemical Stocks for the Biofuel Industry

My NMR results also had immediate implications for the biofuel industry. With concerns over climate and energy security, the biofuels industry is becoming a major consumer of agricultural products. A shift in focus from primarily food to food and biofuels production in agriculture has led to new questions on how to maximize production for biofuel crops. I show that agriculture techniques used to crop for corn, a major biofuel crop, can be altered, and in the process made more sustainable, to maximize for biochemical stocks rather than mass yield, depending on the crops intended use (food or fuel). Both corn grain carbohydrate (fuel) and protein (food) respond nonlinearly to increased N fertilizer, plateauing between 67 – 134 kg N ha^{-1}. When cost-efficiency is considered, cropping grain for food (protein) gives the most returns per dollar between 101 – 134 kg N ha^{-1}, while cropping grain for fuel (carbohydrate) maximizes returns per dollar at 67 kg N ha^{-1}. Cropping grain to be processed into grain ethanol is less than ideal since it removes grain from the food supply.

Alternatively, harvesting crop residue as a secondary commodity for cellulosic ethanol has the potential to meet biofuel feedstock demands without detracting from food supplies. Residue carbohydrate responds modestly and linearly to increasing N fertilizer

(25% increase at the highest fertilization rate 202 kg N ha^{-1}). Though residue carbohydrate responds linearly to increasing N fertilizer, the cost to produce residue carbohydrate plateaus at 67 kg N ha^{-1}. Residue lignin stocks have a stronger response to N fertilizer, increasing 40% with 202 kg N ha^{-1}. To produce a higher quality feedstock for easier conversion to ethanol (high carbohydrate, low lignin concentrations), lower N fertilization rates are needed.

Future Directions

Different crop types will respond differently to N fertilization and likely have different biochemical responses. Even within a crop species, different crop organs have different biochemical responses, as seen with corn. As the biofuels industry moves toward more sustainable feedstocks (i.e. switchgrass, miscanthus, grassland species), it will be critical to understand how these biofuel crops respond to different management techniques, particularly N fertilizer. In addition, to improve the biochemical stocks approach to cropping it will be necessary to improve the faster, more robust remote sensing techniques, specifically near infrared spectroscopy (NIRS). NIRS in field estimations of biochemical composition can be improved through calibration with ^{13}C NMR.

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APPENDIX A

Elemental Analysis Data

Elemental analysis performed at Rice University on a Costech CHNS/O 4100 elemental analyzer at Rice University or a Perkin-Elmer 2400 Series CHNS/O elemental analyzer at the University of California – Santa Barbara's Marine Science Institute. Carbon and nitrogen data were collected for samples being analyzed using ^{13}C NMR and the MMM (the Kellogg Biological Station – Long Term Ecological Research Treatment 1 Crops-Table A1 and the N Rate Experiment-Table A2). Carbon, nitrogen, hydrogen, and oxygen data was collected for the litterbag experiment (Table A3).

TABLES Pg #

Table A1. Kellogg Biological Station Treatment 1 Crop Elemental Analysis Data

Year	Treatment	Replicate	Crop	Organ	Percent Carbon			Percent Nitrogen		
					n	Average	Std Dev	n	Average	Std Dev
2003	T1	R1	Soy	Grain	3	51.49	0.63	3	6.661	0.122
2003	T1	R1	Soy	Stover	4	39.14	0.67	4	2.504	0.071
2003	T1	R2	Soy	Grain	4	51.70	0.49	4	6.440	0.104
2003	T1	R2	Soy	Stover	1	42.40		1	3.123	
2003	T1	R3	Soy	Grain	3	51.42	0.04	3	6.435	0.104
2003	T1	R3	Soy	Stover	1	43.36		1	3.279	
2004	T1	R1	Wheat	Grain	5	41.65	0.72	5	1.529	0.030
2004	T1	R1	Wheat	Stover	3	44.89	0.07	3	0.397	0.031
2004	T1	R2	Wheat	Grain	3	42.63	0.32	3	1.579	0.173
2004	T1	R2	Wheat	Stover	3	43.25	0.27	3	0.535	0.044
2004	T1	R3	Wheat	Grain	4	40.76	0.14	4	1.681	0.037
2004	T1	R3	Wheat	Stover	4	42.90	0.18	4	0.491	0.007
2005	T1	R1	Corn	Grain	2	44.42	0.97	2	1.256	0.059
2005	T1	R1	Corn	Stover	1	46.44		1	0.431	
2005	T1	R2	Corn	Grain	2	44.46	0.25	2	1.528	0.110
2005	T1	R2	Corn	Stover	1	46.54		1	0.519	
2005	T1	R3	Corn	Grain	2	44.83	0.12	2	1.344	0.061
2005	T1	R3	Corn	Stover	1	46.04		1	0.571	

Table A2. Litterbag Experiment Elemental Analysis Data

Bag #	Time (days)	Replicate	Percent Carbon			Percent Hydrogen			Percent Nitrogen			Percent Oxygen		
			n	Average	Std Dev	n	Average	Std Dev	n	Average	Std Dev	n	Average	Std Dev
~	0	~	2	45.10	0.16	2	5.650	0.126	2	1.028	0.047	18	40.25	2.20
1	16	1	2	45.41	0.39	2	5.894	0.140	2	0.484	0.012	18	42.65	1.64
2	16	2	2	45.96	0.46	2	5.622	0.147	2	0.770	0.007	14	40.69	1.86
3	16	3	2	45.86	0.10	2	5.600	0.022	2	0.683	0.005	15	40.26	1.71
4	31	1	2	46.28	0.39	2	5.791	0.165	2	0.745	0.050	12	41.48	1.92
5	31	2	2	46.88	0.26	2	5.711	0.026	2	0.935	0.021	15	41.80	2.11
6	31	3	2	46.57	0.00	2	6.161	0.542	2	0.648	0.079	12	42.60	2.21
7	44	1	2	47.02	0.29	2	6.002	0.019	2	0.851	0.012	12	42.44	1.78
8	44	2	2	48.18	0.05	2	6.023	0.013	2	0.705	0.008	15	42.10	2.17
9	44	3	2	47.53	0.11	2	5.995	0.089	2	0.624	0.036	15	42.12	1.57
10	182	1	2	46.66	3.55	2	5.633	0.381	2	0.919	0.051	15	46.45	6.47
11	182	2	2	44.95	3.69	2	5.437	0.429	2	1.245	0.050	12	41.97	2.90
12	182	3	2	51.67	1.21	2	6.192	0.102	2	0.928	0.016	17	45.03	5.12
13	206	1	2	48.75	1.12	2	5.807	0.195	2	0.794	0.026	12	39.31	5.87
14	206	2	2	44.62	2.84	2	5.380	0.348	2	0.908	0.028	12	40.38	1.96
15	206	3	2	52.33	2.35	2	6.400	0.011	2	1.372	0.278	15	44.30	3.18

Table A3. Elemental Analysis Data for Corn Grain grown under varying N fertilization rates with a Cover Crop

Corn Grain		**Percent Carbon**			**Percent Nitrogen**		
Nitrogen Rate (kg N ha^{-1})	**Replicate**	**n**	**Average**	**Std Dev**	**n**	**Average**	**Std Dev**
0	1	8	43.76	0.58	6	0.836	0.043
0	2	1	42.38		1	0.937	
0	3	1	42.29		1	0.970	
0	4	1	41.60		1	1.184	
34	1	2	43.73	0.05	3	1.014	0.090
34	2	1	43.43		1	1.043	
34	3	1	41.96		1	0.992	
34	4	1	43.12		1	1.109	
67	1	3	44.07	0.35	3	1.068	0.026
67	2	1	41.78		1	1.182	
67	3	1	42.84		1	1.020	
67	4	1	42.26		1	1.009	
101	1	3	44.09	0.30	3	1.121	0.024
101	2	1	42.29		1	1.216	
101	3	1	41.64		1	1.209	
101	4	1	43.38		1	1.234	
134	1	3	44.10	0.27	3	1.203	0.010
134	2	1	43.09		1	1.484	
134	3	1	42.05		1	1.173	
134	4	1	42.55		1	1.407	
168	1	3	43.87	0.41	3	1.169	0.017
168	2	1	42.51		1	1.291	
168	3	1	41.43		1	1.450	
168	4	1	42.85		1	1.411	
202	1	6	44.31	0.17	5	1.290	0.015
202	2	1	41.60		1	1.301	
202	3	1	42.36		1	1.373	
202	4	1	42.29		1	1.252	

Table A3 (cont.). Elemental Analysis Data for Corn Grain grown under varying N fertilization rates without a Cover Crop

Corn Grain		Percent Carbon			Percent Nitrogen		
Nitrogen Rate (kg N ha^{-1})	Replicate	n	Average	Std Dev	n	Average	Std Dev
0	1	5	42.95	1.35	5	0.864	0.044
0	2	3	41.38	0.85	3	0.900	0.060
0	3	3	41.28	0.39	3	0.998	0.102
0	4	3	41.32	0.66	3	0.972	0.111
34	1	1	42.54		1	1.066	
34	2	1	42.30		1	1.073	
34	3	1	41.63		1	1.128	
34	4	1	42.17		1	1.141	
67	1	4	41.95	0.55	2	1.072	0.144
67	2	2	41.67	0.13	2	1.040	0.141
67	3	2	42.06	0.75	2	1.086	0.192
67	4	2	42.01	0.40	2	1.104	0.231
101	1	1	42.49		1	1.175	
101	2	1	42.39		1	1.198	
101	3	1	41.90		1	1.149	
101	4	1	43.33		1	1.303	
134	1	2	42.46	0.36	2	1.116	0.163
134	2	2	42.55	0.79	2	1.173	0.187
134	3	2	42.38	0.22	2	1.155	0.177
134	4	2	42.32	0.20	2	1.238	0.180
168	1	1	42.34		1	1.349	
168	2	1	43.31		1	1.304	
168	3	1	42.27		1	1.286	
168	4	1	43.11		1	1.298	
202	1	4	43.91	0.71	4	1.201	0.094
202	2	3	42.46	0.83	3	1.115	0.148
202	3	2	42.52	0.26	2	1.155	0.191
202	4	3	42.18	0.33	3	1.246	0.171

Table A3 (cont.). Elemental Analysis Data for Corn Leaf & Stem grown under varying N fertilization rates with a Cover Crop

Corn Leaf & Stem		**Percent Carbon**			**Percent Nitrogen**		
Nitrogen Rate ($kg\ N\ ha^{-1}$)	**Replicate**	**n**	**Average**	**Std Dev**	**n**	**Average**	**Std Dev**
0	1	9	44.66	0.16	4	0.346	0.029
0	2	1	42.88		1	0.479	
0	3	1	43.98		1	0.514	
0	4	1	42.51		1	0.432	
34	1	1	44.11		1	0.536	
34	2	1	44.31		1	0.619	
34	3	1	43.68		1	0.583	
34	4	1	43.44		1	0.604	
67	1	3	45.39	0.12	3	0.574	0.015
67	2	1	44.52		1	0.777	
67	3	1	44.42		1	0.767	
67	4	1	44.17		1	0.641	
101	1	6	45.22	0.28	6	0.735	0.097
101	2	1	44.22		1	0.857	
101	3	1	44.65		1	1.022	
101	4	1	45.05		1	0.720	
134	1	6	45.60	0.06	3	0.814	0.025
134	2	1	44.54		1	1.001	
134	3	1	44.48		1	0.860	
134	4	1	44.52		1	1.061	
168	1	6	44.80	0.83	6	0.964	0.072
168	2	1	44.49		1	1.079	
168	3	1	44.12		1	1.045	
168	4	1	44.63		1	1.124	
202	1	3	45.47	0.24	2	0.976	0.006
202	2	1	44.51		1	0.988	
202	3	1	44.76		1	1.017	
202	4	1	44.39		1	0.911	

Table A3 (cont.). Elemental Analysis Data for Corn Leaf & Stem grown under varying N fertilization rates without a Cover Crop

Corn Leaf & Stem		Percent Carbon			Percent Nitrogen		
Nitrogen Rate (kg N ha^{-1})	Replicate	n	Average	Std Dev	n	Average	Std Dev
0	1	5	43.99	1.00	5	0.392	0.027
0	2	5	43.15	0.61	5	0.325	0.037
0	3	3	43.13	1.12	3	0.486	0.132
0	4	3	42.73	0.47	3	0.456	0.132
34	1	2	42.90	1.26	2	0.536	0.078
34	2	1	44.36		1	0.619	
34	3	1	43.18		1	0.650	
34	4	1	44.07		1	0.552	
67	1	2	43.67	0.79	2	0.706	0.150
67	2	2	44.45	0.90	2	0.583	0.018
67	3	2	43.49	0.72	2	0.685	0.091
67	4	2	43.78	1.02	2	0.627	0.095
101	1	2	43.44	1.20	2	0.840	0.098
101	2	1	44.56		1	1.009	
101	3	1	44.63		1	0.710	
101	4	1	44.09		1	0.816	
134	1	3	44.09	0.87	3	0.685	0.061
134	2	2	43.97	1.22	2	0.926	0.107
134	3	2	43.96	1.23	2	0.718	0.088
134	4	2	43.89	1.14	2	0.988	0.167
168	1	2	43.59	1.37	2	0.885	0.021
168	2	1	43.54		1	0.969	
168	3	1	44.51		1	0.787	
168	4	1	44.50		1	0.828	
202	1	5	44.61	1.03	5	0.908	0.039
202	2	2	43.98	1.13	5	0.884	0.147
202	3	2	44.04	1.07	2	0.896	0.035
202	4	2	43.77	0.77	2	1.038	0.180

Table A3 (cont.). Elemental Analysis Data for Corn Reproductive Support grown under varying N fertilization rates with a Cover Crop

Corn Reproductive Support		Percent Carbon			Percent Nitrogen		
Nitrogen Rate (kg N ha^{-1})	Replicate	n	Average	Std Dev	n	Average	Std Dev
0	1	9	45.67	0.72	4	0.333	0.010
0	2	1	44.92		1	0.568	
0	3	1	45.72		1	0.422	
0	4	1	44.75		1	0.667	
34	1	4	45.89	0.22	4	0.512	0.043
34	2	1	44.63		1	0.445	
34	3	1	45.37		1	0.372	
34	4	1	45.67		1	0.490	
67	1	4	45.41	0.20	4	0.475	0.040
67	2	1	44.84		1	0.692	
67	3	1	44.76		1	0.444	
67	4	1	45.24		1	0.495	
101	1	4	45.81	0.20	4	0.498	0.082
101	2	1	45.45		1	0.617	
101	3	1	45.25		1	0.597	
101	4	1	45.25		1	0.565	
134	1	4	45.60	0.44	4	0.517	0.084
134	2	1	44.85		1	0.452	
134	3	1	44.84		1	0.694	
134	4	1	44.88		1	0.634	
168	1	4	45.20	0.42	4	0.477	0.042
168	2	1	45.50		1	0.671	
168	3	1	45.33		1	0.490	
168	4	1	45.14		1	0.623	
202	1	6	45.84	0.19	5	0.490	0.014
202	2	1	45.42		1	0.421	
202	3	1	45.12		1	0.490	
202	4	1	44.76		1	0.628	

Table A3 (cont.). Elemental Analysis Data for Corn Reproductive Support grown under varying N fertilization rates without a Cover Crop

Corn Reproductive Support		Percent Carbon			Percent Nitrogen		
Nitrogen Rate (kg N ha^{-1})	Replicate	n	Average	Std Dev	n	Average	Std Dev
0	1	5	44.84	1.06	5	0.352	0.031
0	2	3	44.03	0.74	3	0.490	0.055
0	3	3	44.23	0.93	3	0.520	0.051
0	4	3	44.19	0.58	3	0.436	0.106
34	1	3	44.67	2.16	2	0.446	0.022
34	2	1	45.44		1	0.560	
34	3	1	45.53		1	0.529	
34	4	1	45.82		1	0.492	
67	1	5	44.19	0.92	3	0.525	0.103
67	2	2	44.40	0.82	2	0.378	0.166
67	3	2	44.52	1.07	2	0.436	0.135
67	4	2	44.31	0.92	2	0.450	0.141
101	1	2	44.34	1.70	2	0.423	0.032
101	2	1	45.28		1	0.582	
101	3	1	45.46		1	0.671	
101	4	1	45.76		1	0.548	
134	1	3	44.47	1.06	3	0.407	0.056
134	2	2	44.36	0.97	2	0.532	0.087
134	3	2	44.80	1.20	2	0.574	0.161
134	4	2	44.37	1.08	2	0.612	0.186
168	1	2	44.41	1.48	2	0.472	0.017
168	2	1	45.01		1	0.505	
168	3	1	44.56		1	0.558	
168	4	1	45.67		1	0.597	
202	1	5	44.81	1.10	5	0.432	0.037
202	2	2	44.49	1.03	2	0.405	0.021
202	3	2	44.06	0.58	2	0.402	0.087
202	4	2	44.01	0.29	2	0.537	0.123

Table A3 (cont.). Summary of Elemental Analysis Data for Corn grown under varying N fertilization rates with a Cover Crop

		Percent Carbon				Percent Nitrogen			
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 1	Rep 2	Rep 3	Rep 4
Grain	0	43.76	42.38	42.29	41.60	0.836	0.937	0.970	1.184
	34	43.73	43.43	41.96	43.12	1.014	1.043	0.992	1.109
	67	44.07	41.78	42.84	42.26	1.068	1.182	1.020	1.009
	101	44.09	42.29	41.64	43.38	1.121	1.216	1.209	1.234
	134	44.10	43.09	42.05	42.55	1.203	1.484	1.173	1.407
	168	43.87	42.51	41.43	42.85	1.169	1.291	1.450	1.411
	202	44.31	41.60	42.36	42.29	1.290	1.301	1.373	1.252
Reproductive Support	0	45.67	44.92	45.72	44.75	0.333	0.568	0.422	0.667
	34	45.89	44.63	45.37	45.67	0.512	0.445	0.372	0.490
	67	45.41	44.84	44.76	45.24	0.475	0.692	0.444	0.495
	101	45.81	45.45	45.25	45.25	0.498	0.617	0.597	0.565
	134	45.60	44.85	44.84	44.88	0.517	0.452	0.694	0.634
	168	45.20	45.50	45.33	45.14	0.477	0.671	0.490	0.623
	202	45.84	45.42	45.12	44.76	0.490	0.421	0.490	0.628
Leaf & Stem	0	44.66	42.88	43.98	42.51	0.346	0.479	0.514	0.432
	34	44.11	44.31	43.68	43.44	0.536	0.619	0.583	0.604
	67	45.39	44.52	44.42	44.17	0.574	0.777	0.767	0.641
	101	45.22	44.22	44.65	45.05	0.735	0.857	1.022	0.720
	134	45.60	44.54	44.48	44.52	0.814	1.001	0.860	1.061
	168	44.80	44.49	44.12	44.63	0.964	1.079	1.045	1.124
	202	45.47	44.51	44.76	44.39	0.976	0.988	1.017	0.911
Crop Residue	0	44.87	43.31	44.36	42.95	0.344	0.498	0.494	0.479
	34	44.50	44.39	44.09	43.98	0.531	0.579	0.532	0.577
	67	45.40	44.60	44.51	44.43	0.552	0.756	0.684	0.605
	101	45.37	44.52	44.81	45.10	0.675	0.798	0.905	0.680
	134	45.60	44.62	44.56	44.62	0.731	0.863	0.820	0.949
	168	44.90	44.74	44.42	44.75	0.841	0.977	0.908	1.003
	202	45.56	44.74	44.85	44.49	0.859	0.844	0.887	0.834
Total Plant	0	44.44	42.91	43.51	42.48	0.535	0.684	0.691	0.724
	34	44.11	43.92	43.01	43.55	0.773	0.807	0.764	0.840
	67	44.68	43.06	43.58	43.28	0.833	0.989	0.871	0.819
	101	44.66	43.23	43.08	44.14	0.920	1.040	1.071	0.990
	134	44.75	43.73	43.13	43.46	0.999	1.225	1.021	1.205
	168	44.33	43.52	42.73	43.70	1.023	1.149	1.214	1.229
	202	44.86	43.00	43.47	43.23	1.102	1.097	1.155	1.073

Table A3 (cont.). Summary of Elemental Analysis Data for Corn grown under varying N fertilization rates without a Cover Crop

		Percent Carbon				Percent Nitrogen			
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 1	Rep 2	Rep 3	Rep 4
Grain	0	42.95	41.38	41.28	41.32	0.864	0.900	0.998	0.972
	34	42.54	42.30	41.63	42.17	1.066	1.073	1.128	1.141
	67	41.95	41.67	42.06	42.01	1.072	1.040	1.086	1.104
	101	42.49	42.39	41.90	43.33	1.175	1.198	1.149	1.303
	134	42.46	42.55	42.38	42.32	1.116	1.173	1.155	1.238
	168	42.34	43.31	42.27	43.11	1.349	1.304	1.286	1.298
	202	43.91	42.46	42.52	42.18	1.201	1.115	1.155	1.246
Reproductive Support	0	44.84	44.03	44.23	44.19	0.352	0.490	0.520	0.436
	34	44.67	45.44	45.53	45.82	0.446	0.560	0.529	0.492
	67	44.19	44.40	44.52	44.31	0.525	0.378	0.436	0.450
	101	44.34	45.28	45.46	45.76	0.423	0.582	0.671	0.548
	134	44.47	44.36	44.80	44.37	0.407	0.532	0.574	0.612
	168	44.41	45.01	44.56	45.67	0.472	0.505	0.558	0.597
	202	44.81	44.49	44.06	44.01	0.432	0.405	0.402	0.537
Leaf & Stem	0	43.99	43.15	43.13	42.73	0.392	0.325	0.486	0.456
	34	42.90	44.36	43.18	44.07	0.536	0.619	0.650	0.552
	67	43.67	44.45	43.49	43.78	0.706	0.583	0.685	0.627
	101	43.44	44.56	44.63	44.09	0.840	1.009	0.710	0.816
	134	44.09	43.97	43.96	43.89	0.685	0.926	0.718	0.988
	168	43.59	43.54	44.51	44.50	0.885	0.969	0.787	0.828
	202	44.61	43.98	44.04	43.77	0.908	0.884	0.896	1.038
Crop Residue	0	44.16	43.32	43.35	43.00	0.384	0.357	0.493	0.452
	34	43.26	44.58	43.66	44.45	0.517	0.607	0.625	0.539
	67	43.78	44.44	43.73	43.90	0.668	0.535	0.627	0.588
	101	43.67	44.74	44.83	44.46	0.731	0.904	0.701	0.756
	134	44.19	44.06	44.14	44.00	0.611	0.842	0.686	0.902
	168	43.80	43.94	44.52	44.77	0.782	0.841	0.731	0.775
	202	44.65	44.10	44.04	43.83	0.810	0.767	0.774	0.922
Total Plant	0	43.63	42.50	42.43	42.29	0.595	0.585	0.717	0.672
	34	42.88	43.40	42.64	43.28	0.806	0.848	0.878	0.849
	67	42.77	42.88	42.80	42.88	0.891	0.820	0.884	0.867
	101	43.00	43.39	43.17	43.82	0.984	1.072	0.955	1.066
	134	43.24	43.18	43.15	43.04	0.888	1.034	0.948	1.093
	168	42.98	43.59	43.28	43.82	1.099	1.100	1.037	1.072
	202	44.24	43.17	43.20	42.92	1.025	0.964	0.985	1.101

APPENDIX B

Molecular Mixing Model Data

Sample information, ^{13}C nuclear magnetic resonance (NMR) spectroscopy input data for the molecular mixing model (MMM) and MMM output from the 4-component model. Solid-state ^{13}C NMR was performed at Rice University using Bruker 200 MHz NMR spectrometer. C-13 NMR cross polarization-magic angle spinning spectra were collected for samples from the Kellogg Biological Station – Long Term Ecological Research Treatment 1 Crops (Table B1) and the N Rate Experiment (Table B2). C-13 NMR direct polarization-magic angle spinning spectra were collected for grain and leaf & stem samples from the N Rate Experiment. Percent C observed (% C_{obs}) is reported for select CP and DP spectra.

Sample Information								
ID	**Year**	**Treatment**	**Replicate**	**Crop**	**Organ**	**%C**	**%N**	**CP C_{obs}**
CG1	2005	1	1	Corn	Grain	44.42	1.26	
CS1	2005	1	1	Corn	Stover	46.44	0.43	
CG2	2005	1	2	Corn	Grain	44.46	1.53	
CS2	2005	1	2	Corn	Stover	46.54	0.52	
CG3	2005	1	3	Corn	Grain	44.83	1.34	
CS3	2005	1	3	Corn	Stover	46.04	0.57	
WG1	2004	1	1	Wheat	Grain	41.65	1.53	
WS1	2004	1	1	Wheat	Stover	44.89	0.40	
WG2	2004	1	2	Wheat	Grain	42.63	1.58	
WS2	2004	1	2	Wheat	Stover	43.25	0.53	
WG3	2004	1	3	Wheat	Grain	40.84	1.68	
WS3	2004	1	3	Wheat	Stover	43.07	0.49	
SG1	2003	1	1	Soy	Grain	51.49	6.66	
SS1	2003	1	1	Soy	Stover	39.14	2.50	
SG2	2003	1	2	Soy	Grain	51.70	6.44	
SS2	2003	1	2	Soy	Stover	42.40	3.12	
SG3	2003	1	3	Soy	Grain	51.42	6.43	
SS3	2003	1	3	Soy	Stover	43.36	3.28	

Molecular Mixing Model Input							
ID	Alkyl C	Methoxyl C	O-alkyl C	O_2-alkyl C	Aromatic C	Phenolic C	Carbonyl
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
CG1	4.67	4.31	72.01	13.77	2.25	0.51	3.09
CS1	4.37	3.97	62.07	14.31	8.38	3.39	3.98
CG2	4.37	3.73	70.92	14.18	3.32	0.62	3.49
CS2	4.36	3.80	60.80	13.86	7.00	4.02	6.32
CG3	4.07	4.22	71.34	13.92	3.47	0.46	2.81
CS3	3.72	3.49	61.64	14.38	8.64	4.57	3.91
WG1	6.38	5.48	70.78	13.30	2.05	0.54	1.95
WS1	4.16	4.93	62.91	14.38	7.19	3.23	3.66
WG2	5.90	5.02	69.92	13.63	2.19	0.34	3.36
WS2	5.12	4.99	62.02	14.13	7.60	3.08	3.44
WG3	6.74	5.36	68.51	13.18	2.62	0.33	3.76
WS3	4.61	5.15	61.80	13.98	7.66	4.31	2.50
SG1	27.16	12.70	34.68	4.64	4.83	0.55	15.85
SS1	17.00	7.63	49.91	9.28	5.91	2.36	8.40
SG2	24.74	12.33	35.95	5.68	6.12	0.84	14.87
SS2	18.15	7.27	50.09	9.17	5.59	1.44	8.55
SG3	26.27	12.42	35.04	5.12	4.93	0.92	15.69
SS3	18.35	7.01	49.52	8.70	6.35	2.02	9.13

4 Component Molecular Mixing Model Output							
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
CG1	88.64	6.63	3.74	1.00	-0.037	0.028	0.065
CS1	76.64	2.26	20.12	0.98	-0.114	0.009	0.070
CG2	87.46	8.07	4.47	0.00	-0.018	0.034	0.062
CS2	75.76	2.72	20.19	1.34	-0.121	0.011	0.072
CG3	87.71	7.03	5.26	0.00	-0.023	0.030	0.057
CS3	76.03	3.02	20.95	0.00	-0.098	0.012	0.060
WG1	87.41	8.65	2.33	1.61	-0.042	0.037	0.090
WS1	77.81	2.14	18.98	1.07	-0.111	0.009	0.066
WG2	86.74	8.75	3.20	1.31	-0.039	0.037	0.084
WS2	76.78	3.01	18.70	1.51	-0.118	0.012	0.083
WG3	85.20	9.78	3.43	1.59	-0.046	0.041	0.098
WS3	76.29	2.78	20.07	0.87	-0.112	0.011	0.075
SG1	45.75	35.65	4.63	13.98	-0.261	0.129	0.783
SS1	63.93	16.47	10.77	8.82	-0.214	0.064	0.341
SG2	47.11	34.04	7.54	11.31	-0.227	0.125	0.688
SS2	64.52	18.97	7.36	9.15	-0.204	0.074	0.362
SG3	46.23	34.39	5.99	13.38	-0.257	0.125	0.750
SS3	63.39	19.53	8.19	8.89	-0.201	0.076	0.371

Sample Information									
ID	**Year**	**Fertilization Rate (kg N ha^{-1})**	**Replicate**	**Cover**	**Organ**	**%C**	**%N**	**CP C_{obs} (%)**	**DP C_{obs} (%)**
Grain 101-1A	2006	0	1	Cover	Grain	43.76	0.84	76.5	
Grain 203-1A	2006	0	2	Cover	Grain	42.38	0.94		
Grain 307-1A	2006	0	3	Cover	Grain	42.29	0.97		
Grain 402-1A	2006	0	4	Cover	Grain	41.60	1.18		
Grain 107-2A	2006	34	1	Cover	Grain	43.73	1.01	75.7	
Grain 106-3A	2006	67	1	Cover	Grain	44.07	1.07	69.5	
Grain 202-3A	2006	67	2	Cover	Grain	41.78	1.18		
Grain 305-3A	2006	67	3	Cover	Grain	42.84	1.02		
Grain 404-3A	2006	67	4	Cover	Grain	42.26	1.01		
Grain 102-4A	2006	101	1	Cover	Grain	44.09	1.12	81.1	
Grain 104-5A	2006	134	1	Cover	Grain	44.10	1.20	84.3	
Grain 205-5A	2006	134	2	Cover	Grain	43.09	1.48		
Grain 302-5A	2006	134	3	Cover	Grain	42.05	1.17		
Grain 407-5A	2006	134	4	Cover	Grain	42.55	1.41		
Grain 103-6A	2006	168	1	Cover	Grain	43.87	1.17	89.7	
Grain 105-7A	2006	202	1	Cover	Grain	44.31	1.29	94.3	
Grain 204-7A	2006	202	2	Cover	Grain	41.60	1.30		
Grain 304-7A	2006	202	3	Cover	Grain	42.36	1.37		
Grain 406-7A	2006	202	4	Cover	Grain	42.29	1.25		

Sample Information

ID	Year	Fertilization Rate (kg N ha^{-1})	Replicate	Cover	Organ	%C	%N	CP C_{obs} (%)	DP C_{obs} (%)
Grain 101-1B	2006	0	1	No Cover	Grain	42.95	0.86	78.9	108.7
Grain 203-1B	2006	0	2	No Cover	Grain	41.38	0.90		
Grain 307-1B	2006	0	3	No Cover	Grain	41.28	1.00		
Grain 402-1B	2006	0	4	No Cover	Grain	41.32	0.97		
Grain 107-2B	2006	34	1	No Cover	Grain	42.54	1.07	89.1	101.0
Grain 106-3B	2006	67	1	No Cover	Grain	41.95	1.07	64.6	98.4
Grain 202-3B	2006	67	2	No Cover	Grain	41.67	1.04		
Grain 305-3B	2006	67	3	No Cover	Grain	42.06	1.09		
Grain 404-3B	2006	67	4	No Cover	Grain	42.01	1.10		
Grain 102-4B	2006	101	1	No Cover	Grain	42.49	1.18	69.5	98.7
Grain 104-5B	2006	134	1	No Cover	Grain	42.46	1.12	69.8	99.7
Grain 205-5B	2006	134	2	No Cover	Grain	42.55	1.17		
Grain 302-5B	2006	134	3	No Cover	Grain	42.38	1.16		
Grain 407-5B	2006	134	4	No Cover	Grain	42.32	1.24		
Grain 103-6B	2006	168	1	No Cover	Grain	42.34	1.35	69.5	111.0
Grain 105-7B	2006	202	1	No Cover	Grain	43.91	1.20	67.5	110.8
Grain 204-7B	2006	202	2	No Cover	Grain	42.46	1.12		
Grain 304-7B	2006	202	3	No Cover	Grain	42.52	1.16		
Grain 406-7B	2006	202	4	No Cover	Grain	42.18	1.25		

Sample Information									
ID	**Year**	**Fertilization Rate (kg N ha^{-1})**	**Replicate**	**Cover**	**Organ**	**%C**	**%N**	**CP C_{obs} (%)**	**DP C_{obs} (%)**
LS 101-1A	2006	0	1	Cover	Leaf & Stem	44.66	0.35	98.0	
LS 203-1A	2006	0	2	Cover	Leaf & Stem	42.88	0.48		
LS 307-1A	2006	0	3	Cover	Leaf & Stem	43.98	0.51		
LS 402-1A	2006	0	4	Cover	Leaf & Stem	42.51	0.43		
LS 107-2A	2006	34	1	Cover	Leaf & Stem	44.11	0.54	99.8	
LS 106-3A	2006	67	1	Cover	Leaf & Stem	45.39	0.57	84.6	
LS 202-3A	2006	67	2	Cover	Leaf & Stem	44.52	0.78		
LS 305-3A	2006	67	3	Cover	Leaf & Stem	44.42	0.77		
LS 404-3A	2006	67	4	Cover	Leaf & Stem	44.17	0.64		
LS 102-4A	2006	101	1	Cover	Leaf & Stem	45.22	0.74	80.4	
LS 104-5A	2006	134	1	Cover	Leaf & Stem	45.60	0.81	73.1	
LS 205-5A	2006	134	2	Cover	Leaf & Stem	44.54	1.00		
LS 302-5A	2006	134	3	Cover	Leaf & Stem	44.48	0.86		
LS 407-5A	2006	134	4	Cover	Leaf & Stem	44.52	1.06		
LS 103-6A	2006	168	1	Cover	Leaf & Stem	44.80	0.96	75.8	
LS 105-7A	2006	202	1	Cover	Leaf & Stem	45.47	0.98	84.1	
LS 204-7A	2006	202	2	Cover	Leaf & Stem	44.51	0.99		
LS 304-7A	2006	202	3	Cover	Leaf & Stem	44.76	1.02		
LS 406-7A	2006	202	4	Cover	Leaf & Stem	44.39	0.91		

Sample Information									
ID	Year	Fertilization Rate (kg N ha^{-1})	Replicate	Cover	Organ	%C	%N	CP C_{obs} (%)	DP C_{obs} (%)
LS 101-1B	2006	0	1	No Cover	Leaf & Stem	43.99	0.39	73.9	73.0
LS 203-1B	2006	0	2	No Cover	Leaf & Stem	43.15	0.32		
LS 307-1B	2006	0	3	No Cover	Leaf & Stem	43.13	0.49		
LS 402-1B	2006	0	4	No Cover	Leaf & Stem	42.73	0.46		
LS 107-2B	2006	34	1	No Cover	Leaf & Stem	42.90	0.54	83.5	70.2
LS 106-3B	2006	67	1	No Cover	Leaf & Stem	43.67	0.71	86.0	60.6
LS 202-3B	2006	67	2	No Cover	Leaf & Stem	44.45	0.58		
LS 305-3B	2006	67	3	No Cover	Leaf & Stem	43.49	0.68		
LS 404-3B	2006	67	4	No Cover	Leaf & Stem	43.78	0.63		
LS 102-4B	2006	101	1	No Cover	Leaf & Stem	43.44	0.84	85.9	79.0
LS 104-5B	2006	134	1	No Cover	Leaf & Stem	44.09	0.69	85.4	67.6
LS 205-5B	2006	134	2	No Cover	Leaf & Stem	43.97	0.93		
LS 302-5B	2006	134	3	No Cover	Leaf & Stem	43.96	0.72		
LS 407-5B	2006	134	4	No Cover	Leaf & Stem	43.89	0.99		
LS 103-6B	2006	168	1	No Cover	Leaf & Stem	43.59	0.89	79.4	62.5
LS 105-7B	2006	202	1	No Cover	Leaf & Stem	44.61	0.91	76.5	200.9
LS 204-7B	2006	202	2	No Cover	Leaf & Stem	43.98	0.88		
LS 304-7B	2006	202	3	No Cover	Leaf & Stem	44.04	0.90		
LS 406-7B	2006	202	4	No Cover	Leaf & Stem	43.77	1.04		

Sample Information (cont.)								
ID	Year	Fertilization Rate (kg N ha^{-1})	Replicate	Cover	Organ	%C	%N	CP C_{obs} (%)
RS 101-1A	2006	0	1	No Cover	Reproductive Support	45.67	0.33	89.6
RS 203-1A	2006	0	2	No Cover	Reproductive Support	44.92	0.57	
RS 307-1A	2006	0	3	No Cover	Reproductive Support	45.72	0.42	
RS 402-1A	2006	0	4	No Cover	Reproductive Support	44.75	0.67	
RS 107-2A	2006	34	1	No Cover	Reproductive Support	45.89	0.51	81.3
RS 106-3A	2006	67	1	No Cover	Reproductive Support	45.41	0.47	78.9
RS 202-3A	2006	67	2	No Cover	Reproductive Support	44.84	0.69	
RS 305-3A	2006	67	3	No Cover	Reproductive Support	44.76	0.44	
RS 404-3A	2006	67	4	No Cover	Reproductive Support	45.24	0.50	
RS 102-4A	2006	101	1	No Cover	Reproductive Support	45.81	0.50	70.1
RS 104-5A	2006	134	1	No Cover	Reproductive Support	45.60	0.52	71.2
RS 205-5A	2006	134	2	No Cover	Reproductive Support	44.85	0.45	
RS 302-5A	2006	134	3	No Cover	Reproductive Support	44.84	0.69	
RS 407-5A	2006	134	4	No Cover	Reproductive Support	44.88	0.63	
RS 103-6A	2006	168	1	No Cover	Reproductive Support	45.20	0.48	79.3
RS 105-7A	2006	202	1	No Cover	Reproductive Support	45.84	0.49	92.0
RS 204-7A	2006	202	2	No Cover	Reproductive Support	45.42	0.42	
RS 304-7A	2006	202	3	No Cover	Reproductive Support	45.12	0.49	
RS 406-7A	2006	202	4	No Cover	Reproductive Support	44.76	0.63	

Sample Information (cont.)								
ID	Year	Fertilization Rate (kg N ha^{-1})	Replicate	Cover	Organ	%C	%N	CP C_{obs} (%)
RS 101-1B	2006	0	1	No Cover	Reproductive Support	44.84	0.35	80.2
RS 203-1B	2006	0	2	No Cover	Reproductive Support	44.03	0.49	
RS 307-1B	2006	0	3	No Cover	Reproductive Support	44.23	0.52	
RS 402-1B	2006	0	4	No Cover	Reproductive Support	44.19	0.44	
RS 107-2B	2006	34	1	No Cover	Reproductive Support	44.67	0.45	78.8
RS 106-3B	2006	67	1	No Cover	Reproductive Support	44.19	0.53	78.7
RS 202-3B	2006	67	2	No Cover	Reproductive Support	44.40	0.38	
RS 305-3B	2006	67	3	No Cover	Reproductive Support	44.52	0.44	
RS 404-3B	2006	67	4	No Cover	Reproductive Support	44.31	0.45	
RS 102-4B	2006	101	1	No Cover	Reproductive Support	44.34	0.42	83.1
RS 104-5B	2006	134	1	No Cover	Reproductive Support	44.47	0.41	72.4
RS 205-5B	2006	134	2	No Cover	Reproductive Support	44.36	0.53	
RS 302-5B	2006	134	3	No Cover	Reproductive Support	44.80	0.57	
RS 407-5B	2006	134	4	No Cover	Reproductive Support	44.37	0.61	
RS 103-6B	2006	168	1	No Cover	Reproductive Support	44.41	0.47	76.9
RS 105-7B	2006	202	1	No Cover	Reproductive Support	44.81	0.43	81.5
RS 204-7B	2006	202	2	No Cover	Reproductive Support	44.49	0.40	
RS 304-7B	2006	202	3	No Cover	Reproductive Support	44.06	0.40	
RS 406-7B	2006	202	4	No Cover	Reproductive Support	44.01	0.54	

Molecular Mixing Model Input (cont.)							
ID	**Alkyl C**	**Methoxyl C**	**O-alkyl C**	**O_2-alkyl C**	**Aromatic C**	**Phenolic C**	**Carbonyl**
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
Grain 101-1A	4.64	5.05	72.25	13.71	1.23	0.27	2.85
Grain 203-1A	4.56	4.64	72.12	13.68	1.61	0.07	3.31
Grain 307-1A	3.33	3.74	71.97	14.36	2.75	0.26	3.58
Grain 402-1A	5.25	4.86	69.21	13.33	2.70	0.93	3.72
Grain 107-2A	5.27	6.58	70.49	13.40	1.13	0.08	3.05
Grain 106-3A	5.77	6.68	69.86	13.03	1.24	0.16	3.26
Grain 202-3A	5.23	4.88	70.98	13.55	1.49	0.27	3.58
Grain 305-3A	4.98	5.13	72.31	13.72	0.94	0.07	2.85
Grain 404-3A	4.59	4.57	72.04	13.82	1.70	0.41	2.86
Grain 102-4A	4.51	5.83	70.29	13.82	2.00	0.06	3.49
Grain 104-5A	5.01	4.54	69.81	13.60	2.33	0.25	4.46
Grain 205-5A	5.47	3.51	71.05	13.89	1.79	0.42	3.86
Grain 302-5A	5.16	3.42	72.23	14.00	1.79	0.07	3.33
Grain 407-5A	4.68	3.00	70.63	14.00	2.51	0.30	4.88
Grain 103-6A	5.75	5.07	69.92	13.42	1.88	0.25	3.72
Grain 105-7A	6.36	5.71	68.35	12.97	1.93	0.17	4.52
Grain 204-7A	5.40	4.82	70.29	13.40	2.06	0.36	3.67
Grain 304-7A	5.96	5.09	68.74	13.17	2.03	0.44	4.56
Grain 406-7A	5.50	5.01	69.73	13.35	2.31	0.30	3.80

ID	Alkyl C	Methoxyl C	O-alkyl C	O_2-alkyl C	Aromatic C	Phenolic C	Carbonyl
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
Grain 101-1B	4.78	4.52	71.12	13.75	1.82	0.58	3.44
Grain 203-1B	3.88	4.06	70.32	13.94	3.04	0.84	3.91
Grain 307-1B	4.61	4.68	71.37	13.77	2.42	0.18	2.96
Grain 402-1B	4.98	5.39	70.98	13.53	1.45	0.15	3.52
Grain 107-2B	4.80	4.86	70.56	13.73	1.96	0.58	3.52
Grain 106-3B	5.05	4.07	71.38	13.92	1.59	0.50	3.48
Grain 202-3B	5.48	5.23	69.87	13.39	1.77	0.26	4.01
Grain 305-3B	4.81	4.63	70.41	13.63	2.28	0.59	3.65
Grain 404-3B	4.76	4.37	71.26	13.82	1.72	0.52	3.54
Grain 102-4B	4.70	4.57	69.58	13.74	2.63	0.25	4.52
Grain 104-5B	4.82	3.90	70.65	13.99	2.28	0.37	3.99
Grain 205-5B	4.80	3.96	70.64	13.91	2.28	0.43	3.97
Grain 302-5B	6.10	4.89	69.70	13.31	1.50	0.18	4.31
Grain 407-5B	5.21	4.24	70.18	13.79	1.84	0.38	4.36
Grain 103-6B	4.88	4.18	70.85	13.83	1.95	0.10	4.22
Grain 105-7B	5.33	3.92	70.04	13.85	2.65	0.26	3.95
Grain 204-7B	4.86	4.74	70.69	13.40	2.21	0.67	3.43
Grain 304-7B	5.68	5.26	69.74	13.38	1.98	0.35	3.61
Grain 406-7B	6.02	5.06	69.73	13.14	1.90	0.38	3.77

Molecular Mixing Model Input (cont.)

Molecular Mixing Model Input (cont.)							
ID	Alkyl C	Methoxyl C	O-alkyl C	O_2-alkyl C	Aromatic C	Phenolic C	Carbonyl
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
LS 101-1A	3.98	3.79	60.81	14.12	8.77	3.63	4.89
LS 203-1A	7.30	5.66	61.14	13.32	5.16	2.70	4.72
LS 307-1A	5.05	4.53	61.29	13.53	8.11	3.04	4.45
LS 402-1A	5.73	5.33	62.98	13.26	6.29	2.44	3.97
LS 107-2A	5.06	4.10	60.24	13.99	7.97	3.96	4.68
LS 106-3A	6.03	5.37	60.18	13.52	7.59	2.45	4.85
LS 202-3A	7.07	4.92	59.65	12.64	6.83	3.41	5.47
LS 305-3A	6.00	4.96	59.00	13.13	8.25	3.42	5.24
LS 404-3A	6.26	4.96	60.94	13.49	7.08	2.96	4.32
LS 102-4A	7.61	5.17	61.00	12.60	6.55	2.74	4.32
LS 104-5A	8.32	5.64	59.93	12.18	6.06	2.24	5.63
LS 205-5A	7.32	4.37	59.22	12.60	7.76	3.39	5.33
LS 302-5A	6.78	3.98	59.30	12.48	8.78	3.30	5.38
LS 407-5A	7.68	4.72	58.77	12.69	7.46	2.99	5.68
LS 103-6A	7.81	4.60	60.25	12.54	7.01	2.47	5.32
LS 105-7A	8.88	6.24	57.95	12.71	6.36	2.90	4.97
LS 204-7A	6.83	5.15	58.66	12.64	7.77	2.94	6.02
LS 304-7A	7.16	5.06	59.00	12.72	7.64	3.08	5.35
LS 406-7A	7.29	5.55	58.50	12.28	7.53	3.13	5.71

Molecular Mixing Model Input (cont.)							
ID	Alkyl C	Methoxyl C	O-alkyl C	O_2-alkyl C	Aromatic C	Phenolic C	Carbonyl
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
LS 101-1B	5.87	4.99	63.77	13.05	6.12	2.07	4.12
LS 203-1B	5.15	5.06	60.70	13.42	7.69	2.81	5.18
LS 307-1B	5.55	5.09	60.33	13.31	7.46	3.32	4.93
LS 402-1B	6.12	5.41	62.33	13.14	5.75	2.58	4.66
LS 107-2B	6.22	4.88	60.27	13.50	7.56	3.26	4.31
LS 106-3B	6.18	4.76	59.67	13.40	7.29	3.44	5.27
LS 202-3B	6.16	5.24	60.15	13.27	7.56	3.54	4.08
LS 305-3B	6.26	5.15	61.13	13.42	6.74	2.89	4.41
LS 404-3B	6.79	5.17	60.11	13.26	7.03	2.92	4.71
LS 102-4B	8.27	6.08	58.94	12.57	6.15	2.92	5.06
LS 104-5B	6.12	5.14	59.68	13.49	7.77	3.37	4.43
LS 205-5B	7.20	5.89	57.49	12.50	7.82	3.18	5.93
LS 302-5B	7.87	6.00	60.28	12.55	5.86	2.79	4.65
LS 407-5B	7.78	5.24	57.35	12.42	8.45	2.88	5.88
LS 103-6B	6.33	4.83	59.55	13.33	7.42	3.12	5.43
LS 105-7B	7.42	5.04	59.15	12.20	7.64	2.95	5.60
LS 204-7B	6.56	4.60	57.40	12.57	8.81	3.28	6.79
LS 304-7B	8.21	6.04	57.99	12.45	7.31	2.75	5.24
LS 406-7B	7.63	5.51	57.04	12.31	8.27	3.11	6.13

Molecular Mixing Model Input (cont.)							
ID	Alkyl C 0-45 ppm	Methoxyl C 45-60 ppm	O-alkyl C 60-95 ppm	O_2-alkyl C 95-110 ppm	Aromatic C 110-145 ppm	Phenolic C 145-165 ppm	Carbonyl 165-215 ppm
RS 101-1A	4.52	4.41	63.42	14.30	6.44	2.77	4.14
RS 203-1A	5.25	4.83	62.32	13.73	6.52	2.40	4.96
RS 307-1A	3.97	4.40	63.12	14.10	7.17	2.48	4.75
RS 402-1A	5.82	4.92	62.03	13.65	6.29	2.87	4.42
RS 107-2A	4.79	4.17	62.57	14.19	6.88	3.02	4.38
RS 106-3A	4.22	3.41	64.04	14.02	6.77	2.33	5.21
RS 202-3A	4.37	4.22	62.42	13.91	6.81	3.18	5.08
RS 305-3A	4.17	3.89	63.70	14.45	6.61	2.54	4.64
RS 404-3A	4.96	4.30	63.43	14.42	6.31	2.47	4.11
RS 102-4A	4.63	3.88	64.41	13.79	6.88	2.22	4.19
RS 104-5A	3.99	3.78	64.70	14.00	6.17	2.27	5.08
RS 205-5A	4.77	3.51	64.59	13.92	6.12	2.41	4.68
RS 302-5A	3.92	3.25	64.13	13.55	7.13	2.79	5.22
RS 407-5A	4.95	3.96	63.77	13.66	6.16	2.50	5.00
RS 103-6A	5.19	3.95	64.08	13.90	5.93	2.36	4.60
RS 105-7A	4.68	4.31	63.32	14.23	6.64	2.94	3.88
RS 204-7A	4.84	4.11	61.52	13.89	7.29	3.18	5.17
RS 304-7A	4.70	4.59	63.44	14.16	6.49	2.27	4.34
RS 406-7A	4.14	4.11	63.21	14.15	6.63	3.03	4.72

Molecular Mixing Model Input (cont.)							
ID	Alkyl C	Methoxyl C	O-alkyl C	O_2-alkyl C	Aromatic C	Phenolic C	Carbonyl
	0-45 ppm	45-60 ppm	60-95 ppm	95-110 ppm	110-145 ppm	145-165 ppm	165-215 ppm
RS 101-1B	5.13	4.66	63.14	13.70	6.45	2.37	4.54
RS 203-1B	5.34	4.80	63.47	13.82	5.98	2.44	4.13
RS 307-1B	5.53	4.97	64.77	14.27	5.00	1.97	3.50
RS 402-1B	4.33	4.35	62.97	14.18	7.23	2.66	4.28
RS 107-2B	4.01	2.99	63.26	14.27	7.63	3.01	4.83
RS 106-3B	5.29	4.06	61.72	13.90	7.72	2.75	4.55
RS 202-3B	4.97	4.43	62.60	14.05	6.57	2.85	4.52
RS 305-3B	4.18	4.03	63.97	14.58	6.61	2.30	4.35
RS 404-3B	3.65	3.71	63.24	14.42	7.85	2.96	4.17
RS 102-4B	3.99	2.97	61.35	13.74	8.60	3.72	5.63
RS 104-5B	3.86	4.00	64.44	14.40	6.68	2.65	3.97
RS 205-5B	5.03	4.52	64.11	13.79	6.04	2.29	4.21
RS 302-5B	4.14	3.65	64.27	14.39	6.26	2.77	4.53
RS 407-5B	4.93	4.45	63.39	13.90	5.92	2.33	5.08
RS 103-6B	5.30	4.47	62.22	13.59	6.63	2.66	5.14
RS 105-7B	4.90	4.19	63.81	13.99	6.67	2.17	4.26
RS 204-7B	3.84	3.44	63.06	14.77	7.35	3.11	4.44
RS 304-7B	4.47	4.53	63.94	14.26	6.20	2.25	4.35
RS 406-7B	4.04	3.77	61.83	14.15	7.86	3.27	5.08

4 Component Molecular Mixing Model Output							
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{ox}**	**N:C**	**alkyl : O-alkyl**
Grain 101-1A	89.11	4.48	4.22	2.19	-0.06	0.02	0.06
Grain 203-1A	88.97	5.18	4.03	1.82	-0.06	0.02	0.06
Grain 307-1A	88.66	5.37	5.62	0.36	-0.03	0.02	0.05
Grain 402-1A	85.75	6.74	6.02	1.48	-0.06	0.03	0.08
Grain 107-2A	87.38	5.46	4.75	2.41	-0.07	0.02	0.07
Grain 106-3A	86.68	5.73	4.83	2.76	-0.08	0.02	0.08
Grain 202-3A	87.93	6.65	3.58	1.83	-0.05	0.03	0.07
Grain 305-3A	89.32	5.57	3.00	2.11	-0.06	0.02	0.07
Grain 404-3A	88.85	5.59	4.01	1.55	-0.05	0.02	0.06
Grain 102-4A	87.10	5.99	5.58	1.33	-0.05	0.03	0.06
Grain 104-5A	86.63	6.44	5.28	1.65	-0.06	0.03	0.07
Grain 205-5A	88.11	8.09	2.42	1.37	-0.04	0.03	0.08
Grain 302-5A	89.23	6.53	2.49	1.75	-0.05	0.03	0.07
Grain 407-5A	87.60	7.78	3.85	0.77	-0.03	0.03	0.07
Grain 103-6A	86.77	6.29	4.53	2.40	-0.07	0.03	0.08
Grain 105-7A	85.20	6.92	5.07	2.81	-0.08	0.03	0.09
Grain 204-7A	87.10	7.37	3.98	1.55	-0.05	0.03	0.08
Grain 304-7A	85.60	7.69	4.66	2.05	-0.06	0.03	0.09
Grain 406-7A	86.47	7.00	4.76	1.77	-0.06	0.03	0.08

4 Component Molecular Mixing Model Output (cont.)					Litter Quality Indices (cont.)		
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
Grain 101-1B	87.91	4.73	5.24	2.12	-0.07	0.02	0.07
Grain 203-1B	86.83	5.12	7.17	0.88	-0.05	0.02	0.06
Grain 307-1B	88.02	5.68	4.89	1.41	-0.05	0.02	0.06
Grain 402-1B	87.87	5.53	4.50	2.10	-0.06	0.02	0.07
Grain 107-2B	87.35	5.90	5.15	1.60	-0.06	0.03	0.07
Grain 106-3B	88.35	6.00	3.77	1.89	-0.06	0.03	0.07
Grain 202-3B	86.74	5.89	4.98	2.39	-0.07	0.02	0.08
Grain 305-3B	87.11	6.08	5.32	1.48	-0.05	0.03	0.07
Grain 404-3B	88.15	6.17	4.16	1.52	-0.05	0.03	0.07
Grain 102-4B	86.35	6.53	5.86	1.26	-0.05	0.03	0.07
Grain 104-5B	87.52	6.18	4.78	1.52	-0.05	0.03	0.07
Grain 205-5B	87.49	6.48	4.66	1.36	-0.05	0.03	0.07
Grain 302-5B	86.72	6.45	3.99	2.84	-0.08	0.03	0.09
Grain 407-5B	87.18	6.89	4.21	1.72	-0.05	0.03	0.07
Grain 103-6B	87.85	7.49	3.53	1.13	-0.04	0.03	0.07
Grain 105-7B	86.84	6.46	4.90	1.81	-0.06	0.03	0.08
Grain 204-7B	87.33	6.18	5.02	1.47	-0.05	0.03	0.07
Grain 304-7B	86.53	6.42	4.82	2.23	-0.07	0.03	0.08
Grain 406-7B	86.55	6.98	4.13	2.34	-0.07	0.03	0.09

4 Component Molecular Mixing Model Output (cont.)					Litter Quality Indices (cont.)		
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
LS 101-1A	75.25	1.89	22.05	0.80	-0.12	0.01	0.07
LS 203-1A	76.58	2.73	16.13	4.55	-0.17	0.01	0.12
LS 307-1A	75.88	2.85	19.68	1.58	-0.12	0.01	0.08
LS 402-1A	78.11	2.47	16.59	2.84	-0.14	0.01	0.09
LS 107-2A	74.84	2.97	20.70	1.48	-0.13	0.01	0.08
LS 106-3A	74.96	3.10	19.28	2.65	-0.14	0.01	0.10
LS 202-3A	74.43	4.29	17.99	3.30	-0.15	0.02	0.12
LS 305-3A	73.38	4.25	20.46	1.90	-0.13	0.02	0.10
LS 404-3A	75.83	3.55	17.95	2.66	-0.14	0.01	0.10
LS 102-4A	75.92	3.77	16.27	4.04	-0.16	0.02	0.12
LS 104-5A	75.00	4.40	15.78	4.81	-0.17	0.02	0.14
LS 205-5A	73.77	5.76	17.79	2.67	-0.14	0.02	0.12
LS 302-5A	73.52	4.76	19.35	2.37	-0.14	0.02	0.11
LS 407-5A	73.48	5.88	17.51	3.13	-0.14	0.02	0.13
LS 103-6A	75.17	5.22	15.94	3.67	-0.15	0.02	0.13
LS 105-7A	72.80	5.32	17.17	4.71	-0.17	0.02	0.15
LS 204-7A	73.23	5.48	18.84	2.45	-0.14	0.02	0.12
LS 304-7A	73.59	5.60	18.16	2.65	-0.14	0.02	0.12
LS 406-7A	72.97	5.07	18.89	3.08	-0.15	0.02	0.12

4 Component Molecular Mixing Model Output (cont.)					Litter Quality Indices (cont.)		
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
LS 101-1B	79.00	2.16	15.62	3.22	-0.14	0.01	0.09
LS 203-1B	75.37	1.84	20.45	2.34	-0.14	0.01	0.08
LS 307-1B	74.98	2.76	19.98	2.28	-0.14	0.01	0.09
LS 402-1B	77.60	2.60	16.45	3.35	-0.15	0.01	0.10
LS 107-2B	74.94	3.06	19.30	2.69	-0.14	0.01	0.10
LS 106-3B	74.44	3.97	19.17	2.42	-0.14	0.02	0.10
LS 202-3B	74.69	3.22	19.59	2.50	-0.14	0.01	0.10
LS 305-3B	76.13	3.85	17.39	2.64	-0.13	0.02	0.10
LS 404-3B	74.96	3.51	18.26	3.27	-0.15	0.01	0.11
LS 102-4B	73.87	4.77	16.94	4.41	-0.17	0.02	0.14
LS 104-5B	74.26	3.82	19.72	2.21	-0.14	0.02	0.10
LS 205-5B	71.84	5.22	20.07	2.87	-0.15	0.02	0.13
LS 302-5B	75.33	4.01	16.28	4.38	-0.16	0.02	0.13
LS 407-5B	71.58	5.59	19.66	3.17	-0.15	0.02	0.14
LS 103-6B	74.35	4.99	18.50	2.16	-0.13	0.02	0.11
LS 105-7B	73.66	5.02	18.11	3.21	-0.15	0.02	0.13
LS 204-7B	71.56	4.98	21.22	2.24	-0.14	0.02	0.11
LS 304-7B	72.53	5.04	18.41	4.03	-0.16	0.02	0.14
LS 406-7B	71.26	5.89	19.91	2.94	-0.15	0.02	0.13

4 Component Molecular Mixing Model Output (cont.)					Litter Quality Indices (cont.)		
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
RS 101-1A	78.71	1.76	17.60	1.93	-0.12	0.01	0.07
RS 203-1A	77.57	3.07	17.17	2.19	-0.13	0.01	0.08
RS 307-1A	78.23	2.23	18.38	1.15	-0.11	0.01	0.06
RS 402-1A	77.25	3.63	16.71	2.41	-0.13	0.01	0.09
RS 107-2A	77.72	2.59	17.97	1.72	-0.12	0.01	0.08
RS 106-3A	79.40	2.54	16.62	1.44	-0.11	0.01	0.07
RS 202-3A	77.56	3.74	17.79	0.91	-0.10	0.02	0.07
RS 305-3A	79.09	2.39	17.14	1.38	-0.11	0.01	0.07
RS 404-3A	78.87	2.65	16.46	2.02	-0.12	0.01	0.08
RS 102-4A	79.62	2.41	16.22	1.75	-0.11	0.01	0.07
RS 104-5A	80.20	2.51	15.93	1.37	-0.10	0.01	0.06
RS 205-5A	80.08	2.43	15.41	2.09	-0.12	0.01	0.07
RS 302-5A	79.26	3.73	16.50	0.51	-0.09	0.02	0.06
RS 407-5A	79.19	3.41	15.55	1.84	-0.11	0.01	0.08
RS 103-6A	79.60	2.45	15.45	2.51	-0.12	0.01	0.08
RS 105-7A	78.53	2.59	17.26	1.62	-0.11	0.01	0.07
RS 204-7A	76.47	2.26	19.37	1.90	-0.13	0.01	0.08
RS 304-7A	78.79	2.63	16.77	1.81	-0.12	0.01	0.07
RS 406-7A	78.47	3.39	17.27	0.86	-0.10	0.01	0.07

4 Component Molecular Mixing Model Output (cont.)					Litter Quality Indices (cont.)		
ID	**Carbohydrate (%)**	**Protein (%)**	**Lignin (%)**	**Lipid (%)**	**C_{OX}**	**N:C**	**alkyl : O-alkyl**
RS 101-1B	78.38	1.90	17.16	2.56	-0.13	0.01	0.08
RS 203-1B	78.86	2.69	15.99	2.46	-0.13	0.01	0.08
RS 307-1B	80.59	2.83	13.81	2.76	-0.12	0.01	0.09
RS 402-1B	78.04	2.39	18.24	1.33	-0.11	0.01	0.07
RS 107-2B	78.31	2.41	18.32	0.96	-0.11	0.01	0.06
RS 106-3B	76.61	2.89	18.56	1.93	-0.13	0.01	0.09
RS 202-3B	77.81	2.06	17.89	2.23	-0.13	0.01	0.08
RS 305-3B	79.40	2.36	16.85	1.39	-0.11	0.01	0.07
RS 404-3B	78.16	2.45	18.93	0.46	-0.10	0.01	0.06
RS 102-4B	75.88	2.32	21.03	0.77	-0.11	0.01	0.07
RS 104-5B	79.74	2.20	17.00	1.06	-0.10	0.01	0.06
RS 205-5B	79.54	2.89	15.48	2.09	-0.12	0.01	0.08
RS 302-5B	79.75	3.09	16.08	1.09	-0.10	0.01	0.06
RS 407-5B	78.92	3.33	15.81	1.94	-0.11	0.01	0.08
RS 103-6B	77.38	2.58	17.61	2.42	-0.13	0.01	0.09
RS 105-7B	79.11	2.33	16.47	2.09	-0.12	0.01	0.08
RS 204-7B	78.21	2.20	18.72	0.88	-0.11	0.01	0.06
RS 304-7B	79.40	2.20	16.56	1.84	-0.12	0.01	0.07
RS 406-7B	76.69	2.96	19.66	0.68	-0.11	0.01	0.07

APPENDIX C

Statistical Analyses

Statistical analyses were performed on data collected from the Kellogg Biological Station-Long Term Ecological Research Treatment 1, the Litterbag Experiment, and the Nitrogen Rate Experiment. Statistical significance was determined using a two-tailed, t-test (two-sampled, unequal variance) to compare between fertilization rates, crop organ, and cover usage where appropriate. A p-value of 0.05 was used as the significance threshold above which results were not treated as statistically significant. When possible more extensive statistical analyses were performed using SAS statistical software, including analysis of variance (ANOVA) and analysis of covariance (ANCOVA).

C1. KBS-LTER Treatment 1 Crops

T-tests

	Soybean	Wheat	Corn
Soybean	X	0.00003	0.00001
Wheat		X	0.01846
Corn			X

	Soybean Grain	Soybean Stover	Wheat Grain	Wheat Stover	Corn Grain	Corn Stover
Soybean Grain	X	0.00202	0.00022	0.00033	0.00053	0.00017
Soybean Stover		X	0.00001	0.00001	0.00002	0.00001
Wheat Grain			X	[redacted]	0.00987	[redacted]
Wheat Stover				X	0.00478	[redacted]
Corn Grain					X	0.01543
Corn Stover						X

C1. KBS-LTER Treatment 1 Crops (cont.)

SAS DATA

```
data kbscrop;
          input type$ organ$ OR;
          cards;
Soybean   Grain    1.148
Soybean   Grain    1.137
Soybean   Grain    1.145
Soybean   Stover   1.095
Soybean   Stover   1.098
Soybean   Stover   1.099
Wheat     Grain    1.034
Wheat     Grain    1.034
Wheat     Grain    1.038
Wheat     Stover   1.034
Wheat     Stover   1.038
Wheat     Stover   1.035
Corn      Grain    1.027
Corn      Grain    1.027
Corn      Grain    1.025
Corn      Stover   1.035
Corn      Stover   1.038
Corn      Stover   1.032
;
```

```
data kbsorgan;
          input typeorgan$ OR;
          cards;
SoybeanGrain    1.148
SoybeanGrain    1.137
SoybeanGrain    1.145
SoybeanStover   1.095
SoybeanStover   1.098
SoybeanStover   1.099
WheatGrain      1.034
WheatGrain      1.034
WheatGrain      1.038
WheatStover     1.034
WheatStover     1.038
WheatStover     1.035
CornGrain       1.027
CornGrain       1.027
CornGrain       1.025
CornStover      1.035
CornStover      1.038
CornStover      1.032
;
```

```
data KBS;
          input crop$ OR;
          cards;
Corn      1.0307
Corn      1.0320
Corn      1.0288
Soybean   1.1086
Soybean   1.1120
Soybean   1.1140
Wheat     1.0337
Wheat     1.0360
Wheat     1.0363
;
```

C1. KBS-LTER Treatment 1 Crops (cont.)

SAS CODE

```
proc glm data = KBS;
	class crop;
	model OR = crop /SS3;
means crop / tukey;
output out = res r=r1 p=p1;
proc univariate normal plot;
	var r1;
proc plot;
	plot r1*p1;
proc glm data = kbscrop;
	class type organ;
	model OR = type | organ /SS3;
means type / tukey;
output out = res r=r1 p=p1;
proc univariate normal plot;
	var r1;
proc plot;
	plot r1*p1;
proc sort data=kbscrop;
	by organ;
proc glm data = kbscrop;
	class type organ;
	model OR = type | organ /SS3;
means organ / tukey;
lsmeans type*organ;
output out = res r=r1 p=p1;
proc univariate normal plot;
	var r1;
proc plot;
	plot r1*p1;
proc glm data=kbsorgan;
	class typeorgan;
	model OR = typeorgan /SS3;
	means typeorgan / tukey;
	output out = res r=r1 p=p1;
proc univariate normal plot;
	var r1;
proc plot;
	plot r1*p1;
run;
```

The SAS System 12:34 Wednesday, October 27, 2010 1

The GLM Procedure

Class Level Information

Class	Levels	Values
crop	3	Corn Soybean Wheat

Number of Observations Read 9
Number of Observations Used 9

The SAS System 12:34 Wednesday, October 27, 2010 2

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.01239620	0.00619810	1540.96	<.0001
Error	6	0.00002413	0.00000402		
Corrected Total	8	0.01242034			

R-Square	Coeff Var	Root MSE	OR Mean
0.998057	0.189359	0.002006	1.059122

Source	DF	Type III SS	Mean Square	F Value	Pr > F

crop	2	0.01239620	0.00619810	1540.96	<.0001

The GLM Procedure

Tukey's Studentized Range (HSD) Test for OR

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	6
Error Mean Square	4.022E-6
Critical Value of Studentized Range	4.33920
Minimum Significant Difference	0.005

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	crop
A	1.111533	3	Soybean
B	1.035333	3	Wheat
B			
B	1.030500	3	Corn

The UNIVARIATE Procedure
Variable: r1

Moments

N	9	Sum Weights	9

Mean	0	Sum Observations	0
Std Deviation	0.00173686	Variance	3.01667E-6
Skewness	-0.4545065	Kurtosis	-0.6652985
Uncorrected SS	0.00002413	Corrected SS	0.00002413
Coeff Variation	.	Std Error Mean	0.00057895

Basic Statistical Measures

Location		Variability	
Mean	0.000000	Std Deviation	0.00174
Median	0.000467	Variance	3.01667E-6
Mode	.	Range	0.00540
		Interquartile Range	0.00260

Tests for Location: Mu0=0

<table>
<tr><th>Test</th><th colspan="2">-Statistic-</th><th colspan="2">-----p Value------</th></tr>
<tr><td>Student's t</td><td>t</td><td>0</td><td>Pr > |t|</td><td>1.0000</td></tr>
<tr><td>Sign</td><td>M</td><td>1.5</td><td>Pr >= |M|</td><td>0.5078</td></tr>
<tr><td>Signed Rank</td><td>S</td><td>0.5</td><td>Pr >= |S|</td><td>1.0000</td></tr>
</table>

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.94521	Pr < W	0.6377
Kolmogorov-Smirnov	D	0.212504	Pr > D	>0.1500
Cramer-von Mises	W-Sq	0.058918	Pr > W-Sq	>0.2500
Anderson-Darling	A-Sq	0.316457	Pr > A-Sq	>0.2500

Quantiles (Definition 5)

Quantile	Estimate
100% Max	0.002466667
99%	0.002466667
95%	0.002466667
90%	0.002466667
75% Q3	0.000966667
50% Median	0.000466667
25% Q1	-0.001633333
10%	-0.002933333

The UNIVARIATE Procedure
Variable: r1

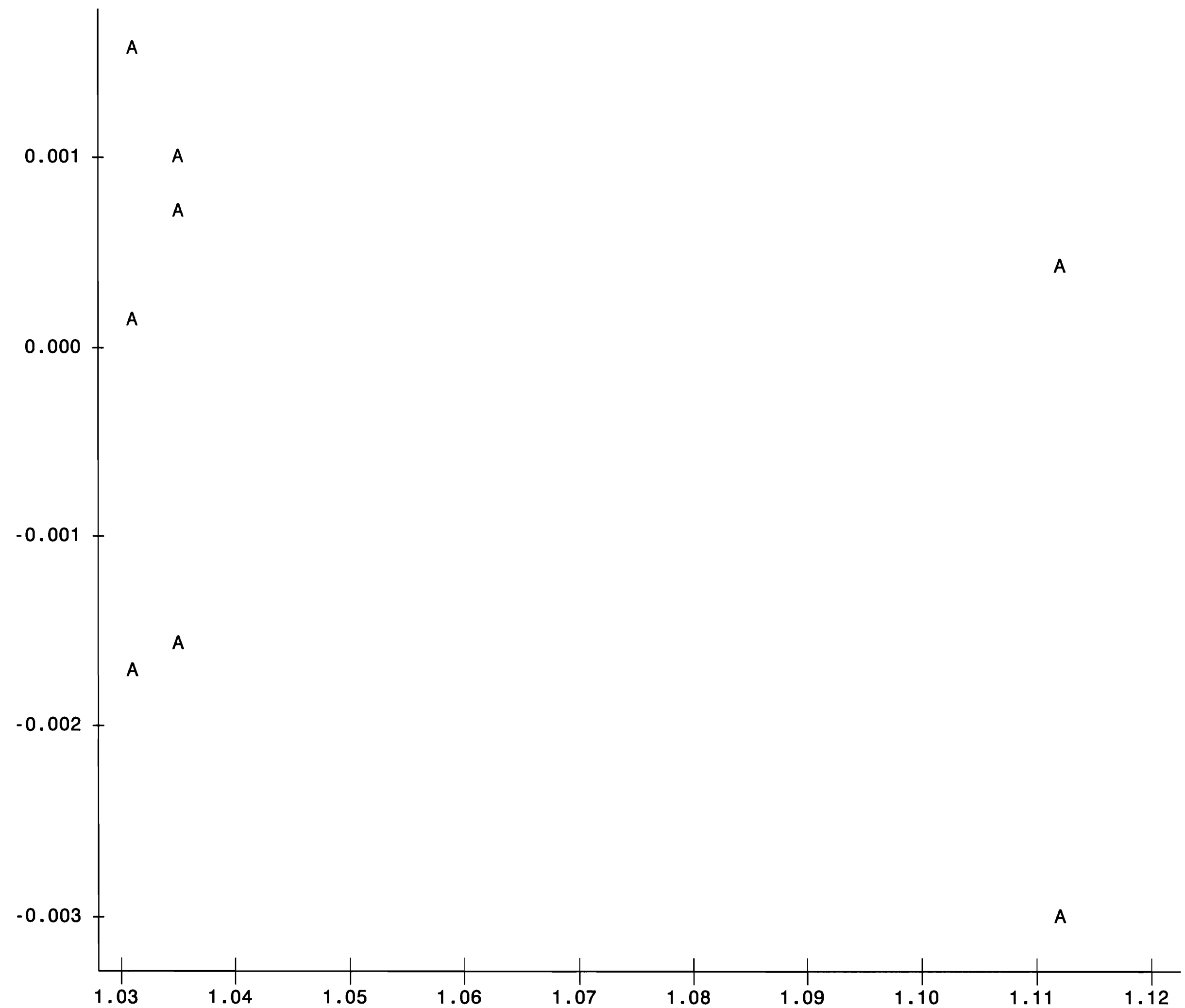
Quantiles (Definition 5)

Quantile	Estimate
5%	-0.002933333
1%	-0.002933333
0% Min	-0.002933333

Extreme Observations

--------Lowest-------		-------Highest-------	
Value	Obs	Value	Obs
-0.002933333	4	0.000466667	5
-0.001700000	3	0.000666667	8
-0.001633333	7	0.000966667	9
0.000200000	1	0.001500000	2
0.000466667	5	0.002466667	6

```
                  Stem Leaf                     #             Boxplot
                     2 5                        1                |
                     1 05                       2             +-----+
                     0 257                      3             *--+--*
                    -0                                        |     |
                    -1 76                       2             +-----+
                    -2 9                        1                |
                       ----+----+----+----+
                   Multiply Stem.Leaf by 10**-3


                                Normal Probability Plot
              0.0025+                                    +++*++
                    |                              +++*++
                    |                     *  *++*++*
                    |                   +++++
                    |             ++*++*
             -0.0025+       ++*+++
                     +----+----+----+----+----+----+----+----+----+----+
                         -2        -1         0        +1        +2


                                The SAS System       12:34 Wednesday, October 27, 2010   6

                 Plot of r1*p1.  Legend: A = 1 obs, B = 2 obs, etc.

    r1 |
       |
 0.003 +
       |
       |
       |                                                             A
       |
       |
 0.002 +
       |
```



0.001
0.000
-0.001
-0.002
-0.003
A
1.03
1.04
1.05
1.06
1.07
1.08
1.09
1.10
1.11
1.12

p1

The GLM Procedure

Class Level Information

Class	Levels	Values
type	3	Corn Soybean Wheat
organ	2	Grain Stover

Number of Observations Read	18
Number of Observations Used	18

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	0.03380717	0.00676143	715.92	<.0001
Error	12	0.00011333	0.00000944		
Corrected Total	17	0.03392050			

R-Square	Coeff Var	Root MSE	OR Mean
0.996659	0.289331	0.003073	1.062167

Source	DF	Type III SS	Mean Square	F Value	Pr > F
type	2	0.03052033	0.01526017	1615.78	<.0001
organ	1	0.00068450	0.00068450	72.48	<.0001
type*organ	2	0.00260233	0.00130117	137.77	<.0001

The GLM Procedure

Tukey's Studentized Range (HSD) Test for OR

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	12
Error Mean Square	9.444E-6
Critical Value of Studentized Range	3.77293
Minimum Significant Difference	0.0047

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	type
A	1.120333	6	Soybean
B	1.035500	6	Wheat
C	1.030667	6	Corn

The UNIVARIATE Procedure

Variable: r1

Moments

N	18	Sum Weights	18
Mean	0	Sum Observations	0
Std Deviation	0.00258199	Variance	6.66667E-6
Skewness	-0.5202897	Kurtosis	0.89217647
Uncorrected SS	0.00011333	Corrected SS	0.00011333
Coeff Variation	.	Std Error Mean	0.00060858

Basic Statistical Measures

Location		Variability	
Mean	0.00000	Std Deviation	0.00258
Median	0.00033	Variance	6.66667E-6
Mode	-0.00133	Range	0.01100
		Interquartile Range	0.00300

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	0	Pr > |t|	1.0000
Sign	M	0.5	Pr >= |M|	1.0000
Signed Rank	S	3	Pr >= |S|	0.8990

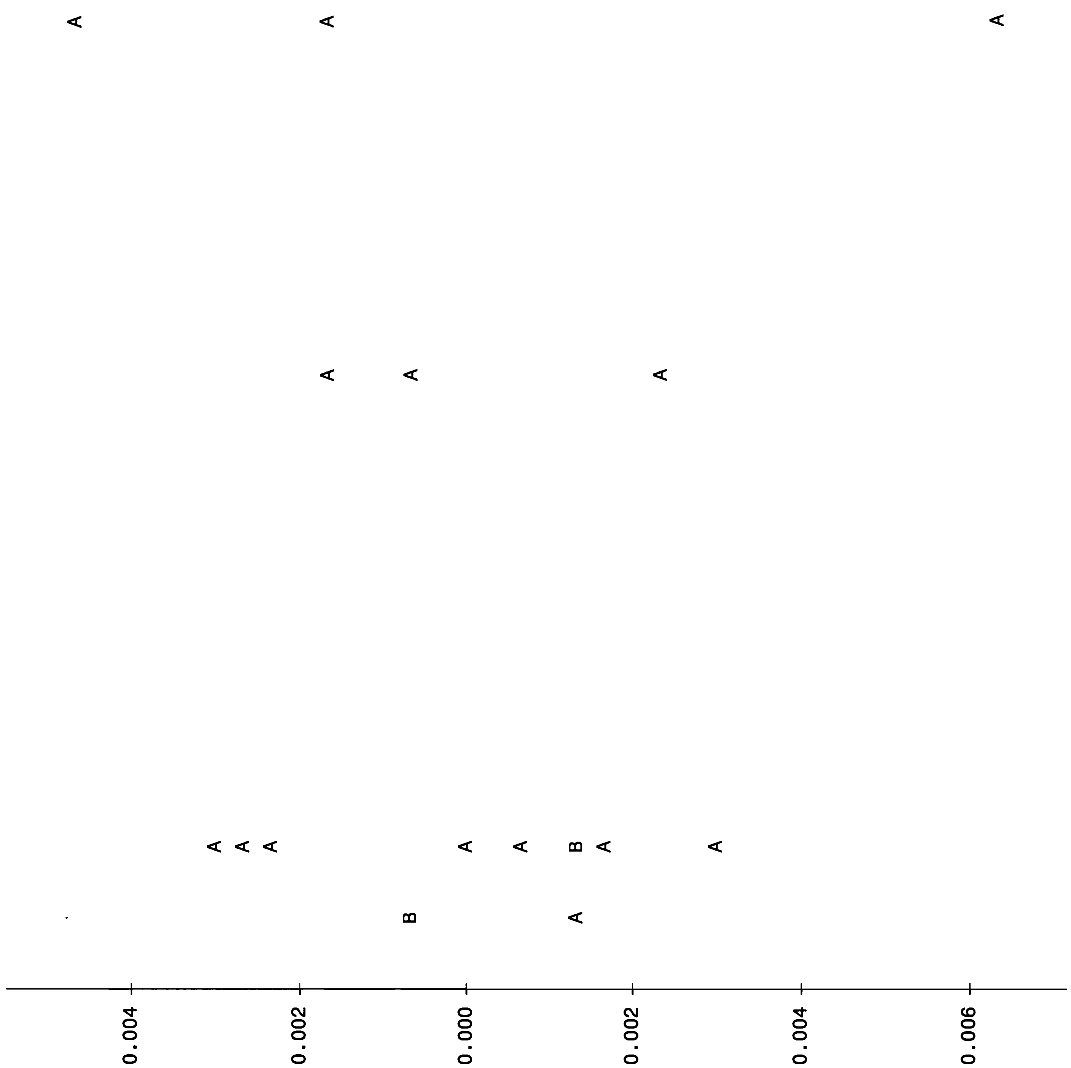
Tests for Normality

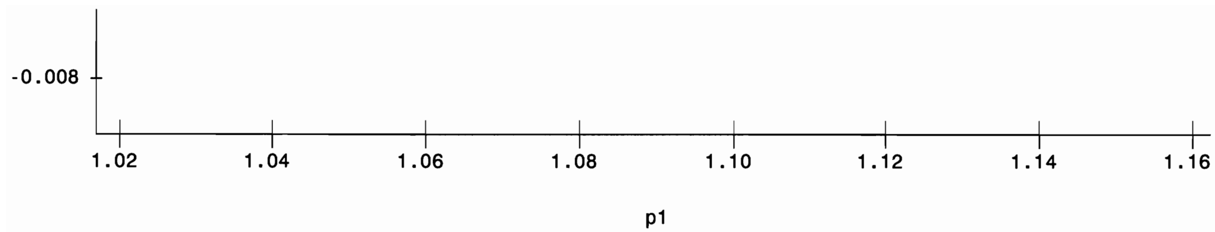
Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.971424	Pr < W	0.8240
Kolmogorov-Smirnov	D	0.101873	Pr > D	>0.1500
Cramer-von Mises	W-Sq	0.031378	Pr > W-Sq	>0.2500

```
Anderson-Darling      A-Sq    0.2307    Pr > A-Sq  >0.2500


                 Quantiles (Definition 5)

                Quantile          Estimate

                100% Max       0.004666667
                99%            0.004666667
                95%            0.004666667
                90%            0.003000000
                75% Q3         0.001666667
                50% Median     0.000333333
                25% Q1        -0.001333333
                10%           -0.003000000

                     The SAS System       12:34 Wednesday, October 27, 2010  11

                 The UNIVARIATE Procedure
                      Variable:  r1

                 Quantiles (Definition 5)

                Quantile          Estimate

                5%            -0.006333333
                1%            -0.006333333
                0% Min        -0.006333333


                   Extreme Observations

     -------Lowest-------        -------Highest------

           Value      Obs             Value      Obs

     -0.00633333        2        0.00166667        6
     -0.00300000       18        0.00233333       11
```

```
-0.00233333       4       0.00266667       9
-0.00166667      10       0.00300000      17
-0.00133333      15       0.00466667       1


Stem Leaf                     #             Boxplot
   4 7                        1                |
   2 370                      3                |
   0 077777                   6             +--+--+
  -0 73337                    5             +-----+
  -2 03                       2                |
  -4
  -6 3                        1                0
     ----+----+----+----+
 Multiply Stem.Leaf by 10**-3


                  Normal Probability Plot
 0.005+                                        ++*+++++
      |                                ++*+*++
      |                        *+**+**+*
-0.001+                 **+**+*+
      |          ++*+*+++
      |  ++++++++
-0.007+++     *
       +----+----+----+----+----+----+----+----+----+----+
           -2        -1         0        +1        +2
```

```
                  The SAS System       12:34 Wednesday, October 27, 2010  12

   Plot of r1*p1.  Legend: A = 1 obs, B = 2 obs, etc.

   r1 |
      |
0.006 +
      |
```


0.004
0.002
0.000
-0.002
-0.004
-0.006



The GLM Procedure

Class Level Information

Class	Levels	Values
type	3	Corn Soybean Wheat
organ	2	Grain Stover

Number of Observations Read	18
Number of Observations Used	18

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	0.03380717	0.00676143	715.92	<.0001
Error	12	0.00011333	0.00000944		

Corrected Total	17	0.03392050			

R-Square	Coeff Var	Root MSE	OR Mean
0.996659	0.289331	0.003073	1.062167

Source	DF	Type III SS	Mean Square	F Value	Pr > F
type	2	0.03052033	0.01526017	1615.78	<.0001
organ	1	0.00068450	0.00068450	72.48	<.0001
type*organ	2	0.00260233	0.00130117	137.77	<.0001

The SAS System 12:34 Wednesday, October 27, 2010 15

The GLM Procedure

Tukey's Studentized Range (HSD) Test for OR

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	12
Error Mean Square	9.444E-6
Critical Value of Studentized Range	3.08131
Minimum Significant Difference	0.0032

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	organ
A	1.068333	9	Grain

B	1.056000	9	Stover

The GLM Procedure
Least Squares Means

type	organ	OR LSMEAN
Corn	Grain	1.02633333
Corn	Stover	1.03500000
Soybean	Grain	1.14333333
Soybean	Stover	1.09733333
Wheat	Grain	1.03533333
Wheat	Stover	1.03566667

The UNIVARIATE Procedure
Variable: r1

Moments

N	18	Sum Weights	18
Mean	0	Sum Observations	0
Std Deviation	0.00258199	Variance	6.66667E-6
Skewness	-0.5202897	Kurtosis	0.89217647
Uncorrected SS	0.00011333	Corrected SS	0.00011333
Coeff Variation	.	Std Error Mean	0.00060858

Basic Statistical Measures

Location		Variability	
Mean	0.00000	Std Deviation	0.00258
Median	0.00033	Variance	6.66667E-6
Mode	-0.00133	Range	0.01100

Interquartile Range 0.00300

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	0	Pr > |t|	1.0000
Sign	M	0.5	Pr >= |M|	1.0000
Signed Rank	S	3	Pr >= |S|	0.8990

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.971424	Pr < W	0.8240
Kolmogorov-Smirnov	D	0.101873	Pr > D	>0.1500
Cramer-von Mises	W-Sq	0.031378	Pr > W-Sq	>0.2500
Anderson-Darling	A-Sq	0.2307	Pr > A-Sq	>0.2500

Quantiles (Definition 5)

Quantile	Estimate
100% Max	0.004666667
99%	0.004666667
95%	0.004666667
90%	0.003000000
75% Q3	0.001666667
50% Median	0.000333333
25% Q1	-0.001333333
10%	-0.003000000

The SAS System 12:34 Wednesday, October 27, 2010 18

The UNIVARIATE Procedure

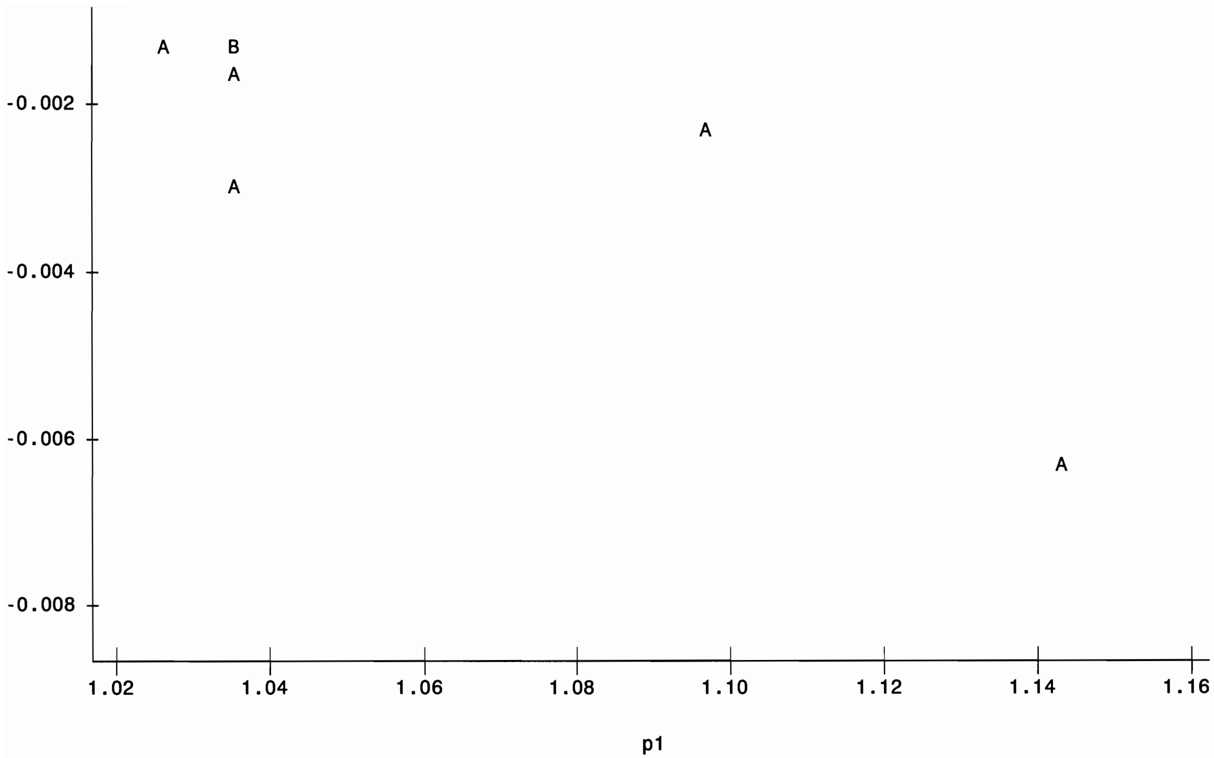
```
                    Variable:  r1

               Quantiles (Definition 5)

              Quantile          Estimate

              5%            -0.006333333
              1%            -0.006333333
              0% Min        -0.006333333


                 Extreme Observations

   -------Lowest-------        -------Highest------

        Value      Obs            Value      Obs

   -0.00633333       2        0.00166667       12
   -0.00300000      18        0.00233333       14
   -0.00233333      10        0.00266667        6
   -0.00166667      13        0.00300000       17
   -0.00133333       9        0.00466667        1


   Stem Leaf                    #             Boxplot
      4 7                       1                |
      2 370                     3                |
      0 077777                  6             +--+--+
     -0 73337                   5             +-----+
     -2 03                      2                |
     -4
     -6 3                       1                0
        ----+----+----+----+
    Multiply Stem.Leaf by 10**-3


                    Normal Probability Plot
0.005+                                        ++*+++++
```

```
       |                                   *++*+*++
       |                          *+**+**+*
-0.001+                   **+**+*+
       |           ++*+*+++
       |  ++++++++
-0.007+++      *
        +----+----+----+----+----+----+----+----+----+----+
            -2        -1         0        +1        +2
```

The SAS System   12:34 Wednesday, October 27, 2010 19

Plot of r1*p1. Legend: A = 1 obs, B = 2 obs, etc.

```
  r1 |
0.006 +
     |
     |
     |                                                        A
     |
0.004 +
     |
     |         A
     |         A
     |         A
0.002 +
     |                             A                          A
     |
     |    B                        A
     |
0.000 +        A
     |
     |         A
```



The SAS System 12:34 Wednesday, October 27, 2010 20

The GLM Procedure

Class Level Information

Class	Levels	Values
typeorgan	6	CornGrai CornStov SoybeanG SoybeanS WheatGra WheatSto

Number of Observations Read 18
Number of Observations Used 18

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	0.03380717	0.00676143	715.92	<.0001
Error	12	0.00011333	0.00000944		
Corrected Total	17	0.03392050			

R-Square	Coeff Var	Root MSE	OR Mean
0.996659	0.289331	0.003073	1.062167

Source	DF	Type III SS	Mean Square	F Value	Pr > F
typeorgan	5	0.03380717	0.00676143	715.92	<.0001

The GLM Procedure

Tukey's Studentized Range (HSD) Test for OR

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	12
Error Mean Square	9.444E-6
Critical Value of Studentized Range	4.75023
Minimum Significant Difference	0.0084

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	typeorgan
A	1.143333	3	SoybeanG
B	1.097333	3	SoybeanS
C	1.035667	3	WheatSto
C			
C	1.035333	3	WheatGra
C			
C	1.035000	3	CornStov
D	1.026333	3	CornGrai

The UNIVARIATE Procedure
Variable: r1

Moments

N	18	Sum Weights	18
Mean	0	Sum Observations	0
Std Deviation	0.00258199	Variance	6.66667E-6
Skewness	-0.5202897	Kurtosis	0.89217647
Uncorrected SS	0.00011333	Corrected SS	0.00011333
Coeff Variation	.	Std Error Mean	0.00060858

Basic Statistical Measures

Location		Variability	
Mean	0.00000	Std Deviation	0.00258
Median	0.00033	Variance	6.66667E-6
Mode	-0.00133	Range	0.01100
		Interquartile Range	0.00300

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	0	Pr > |t|	1.0000
Sign	M	0.5	Pr >= |M|	1.0000
Signed Rank	S	3	Pr >= |S|	0.8990

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.971424	Pr < W	0.8240
Kolmogorov-Smirnov	D	0.101873	Pr > D	>0.1500
Cramer-von Mises	W-Sq	0.031378	Pr > W-Sq	>0.2500
Anderson-Darling	A-Sq	0.2307	Pr > A-Sq	>0.2500

Quantiles (Definition 5)

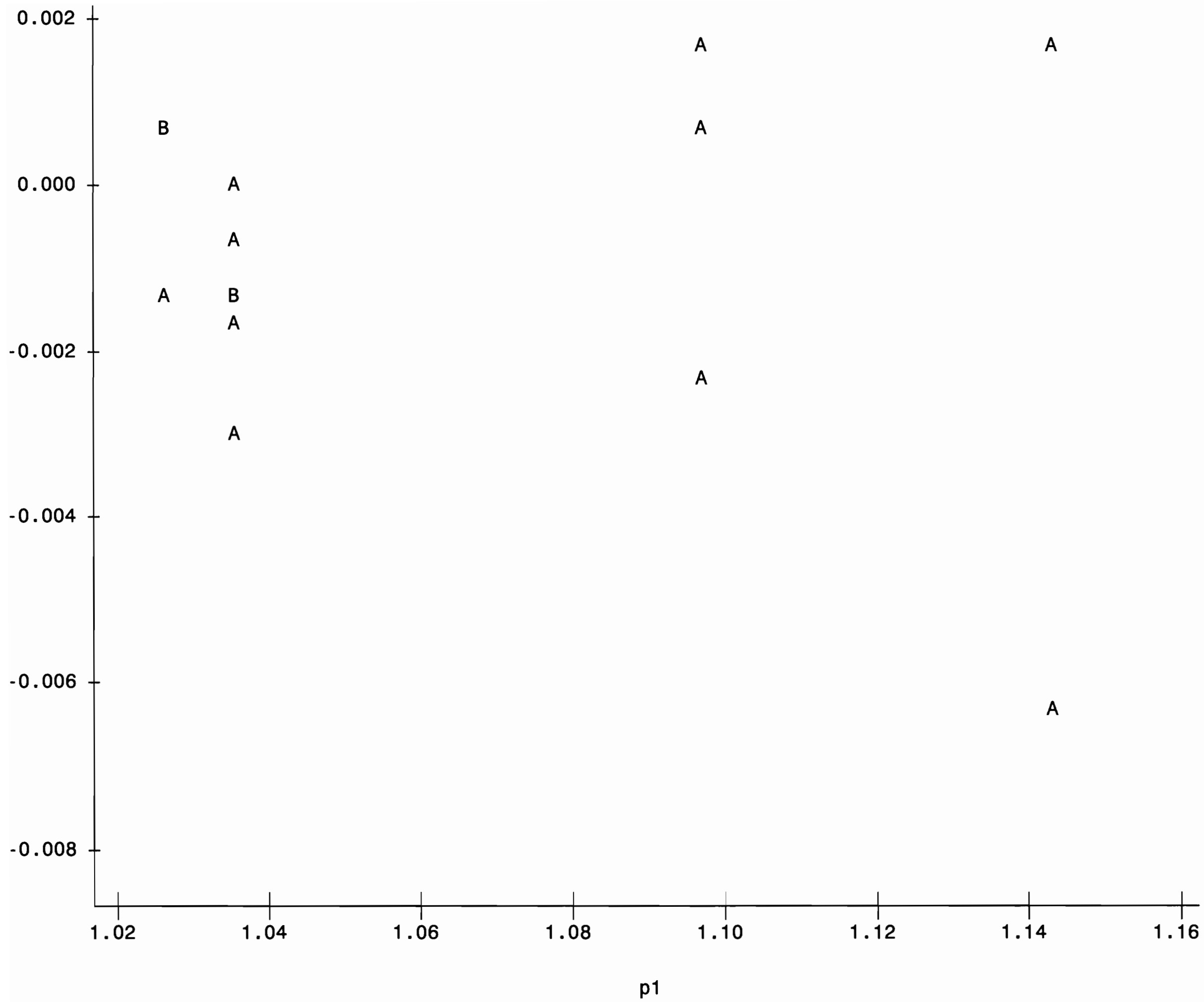
Quantile	Estimate
100% Max	0.004666667
99%	0.004666667
95%	0.004666667

```
                     90%              0.003000000
                     75% Q3           0.001666667
                     50% Median       0.000333333
                     25% Q1          -0.001333333
                     10%             -0.003000000

                           The SAS System       12:34 Wednesday, October 27, 2010  24

                      The UNIVARIATE Procedure
                           Variable:  r1

                      Quantiles (Definition 5)

                     Quantile          Estimate

                     5%              -0.006333333
                     1%              -0.006333333
                     0% Min          -0.006333333


                        Extreme Observations

           -------Lowest-------        -------Highest------

                 Value      Obs              Value      Obs

           -0.00633333        2         0.00166667        6
           -0.00300000       18         0.00233333       11
           -0.00233333        4         0.00266667        9
           -0.00166667       10         0.00300000       17
           -0.00133333       15         0.00466667        1


           Stem Leaf                     #             Boxplot
              4 7                        1                |
              2 370                      3                |
              0 077777                   6             +--+--+
             -0 73337                    5             +-----+
```

```
   -2 03                    2              |
   -4
   -6 3                     1              0
      ----+----+----+----+
  Multiply Stem.Leaf by 10**-3


                Normal Probability Plot
 0.005+                                        ++*+++++
      |                                ++*+*+++
      |                        *+***+**+*
-0.001+                 **+***+*+
      |          ++*+*+++
      |  ++++++++
-0.007+++     *
       +----+----+----+----+----+----+----+----+----+----+
           -2        -1         0        +1        +2
```



```
   Plot of r1*p1.  Legend: A = 1 obs, B = 2 obs, etc.

    r1 |
       |
 0.006 +
       |
       |
       |
       |                                                               A
       |
 0.004 +
       |
       |
       |          A
       |          A
       |          A
```


0.002
0.000
-0.002
-0.004
-0.006
-0.008
1.02
1.04
1.06
1.08
1.10
1.12
1.14
1.16
p1
A
B

C2. Litterbag Experiment

T-tests

Remaining Biomass OR

	t1	t2	T3	t4	t5
t1	X	0.529	**0.001**	0.189	0.616
t2		X	0.560	0.128	0.941
t3			X	0.113	0.755
t4				X	0.134
t5					X

OR_{ba}

	t1	t2	t3	t4	t5
t1	X	0.778	0.234	0.072	0.776
t2		X	0.206	0.145	0.967
t3			X	**0.012**	0.134
t4				X	0.086
t5					X

C2. Litterbag Experiment (cont.)

SAS DATA

```
data Litterbag;
        input time OR;
        cards;
16      0.9704
16      1.0557
16      1.0234
31      1.0143
31      1.0859
31      0.9846
44      0.9964
44      0.9833
44      0.9407
182     1.1174
182     1.1191
182     1.0538
206     0.9925
206     1.0681
206     1.0193
;
```

C2. Litterbag Experiment (cont.)

SAS CODE

```
proc glm data = Litterbag;
        model OR = time /SS3;
        output out = res r=r1 p=p1;
proc univariate normal plot;
        var r1;
proc plot;
        plot r1*p1;
run;
```

The GLM Procedure

Number of Observations Read	15
Number of Observations Used	15

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.00825238	0.00825238	3.37	0.0892
Error	13	0.03179499	0.00244577		
Corrected Total	14	0.04004737			

R-Square	Coeff Var	Root MSE	OR Mean
0.206065	4.809241	0.049455	1.028327

Source	DF	Type III SS	Mean Square	F Value	Pr > F
time	1	0.00825238	0.00825238	3.37	0.0892

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	1.000593889	0.01977353	50.60	<.0001

```
time            0.000289486      0.00015760       1.84      0.0892

                          The SAS System       12:49 Wednesday, October 27, 2010   3

                     The UNIVARIATE Procedure
                          Variable:  r1

                             Moments

 N                            15    Sum Weights                 15
 Mean                          0    Sum Observations             0
 Std Deviation        0.04765575    Variance            0.00227107
 Skewness             0.21061682    Kurtosis            -0.9855144
 Uncorrected SS       0.03179499    Corrected SS        0.03179499
 Coeff Variation               .    Std Error Mean      0.01230466


                    Basic Statistical Measures

          Location                    Variability

      Mean     0.000000     Std Deviation            0.04766
      Median   0.000520     Variance                 0.00227
      Mode      .           Range                    0.14896
                            Interquartile Range      0.08530


                    Tests for Location: Mu0=0

         Test           -Statistic-    -----p Value------

         Student's t    t         0    Pr > |t|    1.0000
         Sign           M       0.5    Pr >= |M|   1.0000
         Signed Rank    S        -1    Pr >= |S|   0.9780


                       Tests for Normality
```

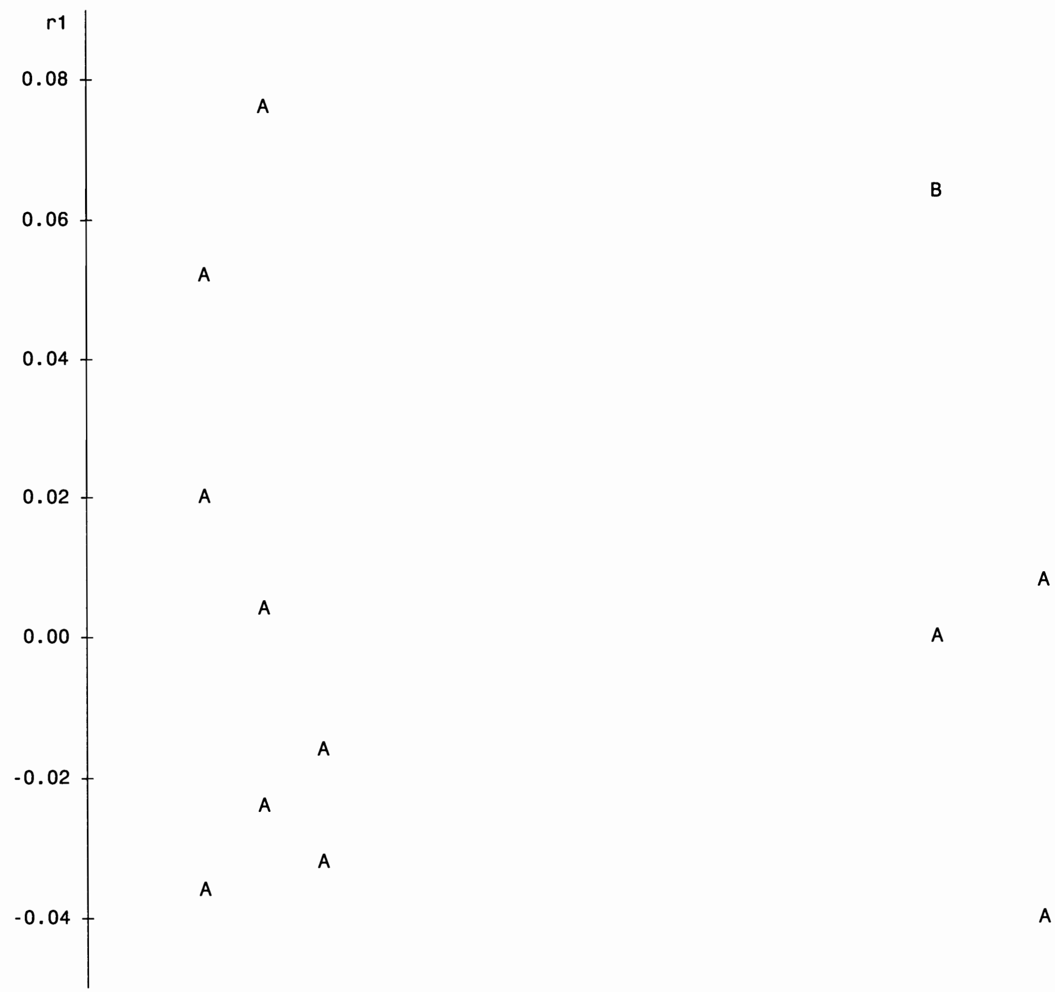
```
Test                  --Statistic---    -----p Value------

Shapiro-Wilk          W     0.946231    Pr < W      0.4672
Kolmogorov-Smirnov    D       0.1219    Pr > D     >0.1500
Cramer-von Mises      W-Sq   0.04125    Pr > W-Sq  >0.2500
Anderson-Darling      A-Sq  0.297297    Pr > A-Sq  >0.2500


                 Quantiles (Definition 5)

                Quantile          Estimate

                100% Max       0.076332039
                99%            0.076332039
                95%            0.076332039
                90%            0.065819623
                75% Q3         0.050474332
                50% Median     0.000519623
                25% Q1        -0.034825668
                10%           -0.067728046

                      The SAS System       12:49 Wednesday, October 27, 2010   4

                 The UNIVARIATE Procedure
                      Variable:  r1

                 Quantiles (Definition 5)

                Quantile          Estimate

                5%            -0.072631281
                1%            -0.072631281
                0% Min        -0.072631281


                   Extreme Observations

      -------Lowest------        ------Highest------
```

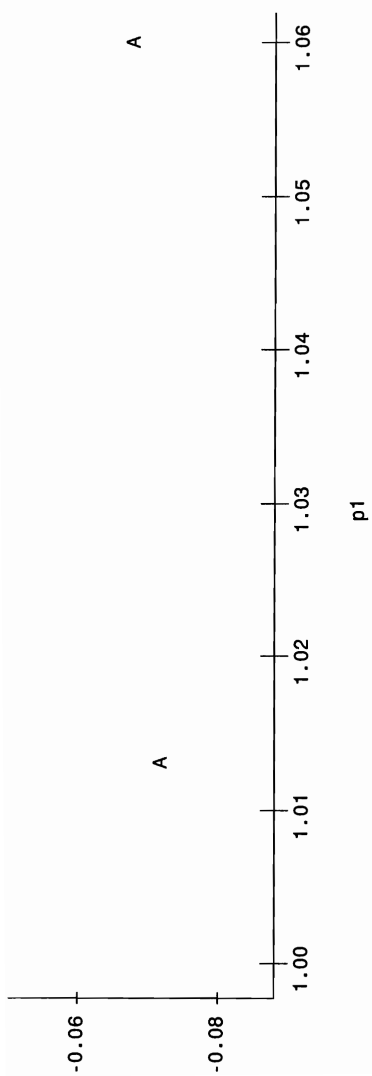
Value	Obs	Value	Obs
-0.0726313	9	0.0181743	3
-0.0677280	13	0.0504743	2
-0.0409280	15	0.0641196	10
-0.0348257	1	0.0658196	11
-0.0300313	8	0.0763320	5

```
 Stem Leaf                     #             Boxplot
    6 466                      3                |
    4 0                        1             +-----+
    2                                        |     |
    0 1588                     4             *--+--*
   -0 7                        1             |     |
   -2 505                      3             +-----+
   -4 1                        1                |
   -6 38                       2                |
      ----+----+----+----+
  Multiply Stem.Leaf by 10**-2
```

```
                  Normal Probability Plot
 0.07+                                  *  *+++++*
     |                                * ++++
     |                              ++++
     |                         *+**+*
     |                     ++*+
     |                 ++*+ *
     |             +++*
-0.07+        *++++*
      +----+----+----+----+----+----+----+----+----+----+
          -2        -1         0        +1        +2
```

Plot of r1*p1. Legend: A = 1 obs, B = 2 obs, etc.




-0.06
-0.08
1.00
1.01
1.02
1.03
1.04
1.05
1.06
p1
A
A

C3. N Rate Experiment Oxidative Ratio

T-tests

Grain OR

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	**67**	**134**	**202**	**0**	**67**	**134**	**202**
Cover Crop	**0**	X	0.26	0.29	***0.03***	0.62	0.27	0.17	***0.09***
	67		X	0.76	0.11	0.35	0.85	0.73	0.43
	134			X	***0.04***	0.30	0.89	0.46	0.16
	202				X	***0.02***	***0.05***	0.18	0.26
No Cover Crop	**0**					X	0.32	0.19	***0.06***
	67						X	0.55	0.24
	134							X	0.67
	202								X

Reproductive Support OR

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	**67**	**134**	**202**	**0**	**67**	**134**	**202**
Cover Crop	**0**	X	0.26	0.19	0.48	0.97	0.42	0.23	0.20
	67		X	0.63	0.45	0.10	0.89	0.76	0.70
	134			X	0.30	0.09	0.67	0.92	0.86
	202				X	0.33	0.76	0.42	0.30
No Cover Crop	**0**					X	0.37	0.15	***0.07***
	67						X	0.74	0.73
	134							X	0.97
	202								X

Leaf & Stem OR

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	**67**	**134**	**202**	**0**	**67**	**134**	**202**
Cover Crop	**0**	X	0.26	***0.05***	***0.04***	0.82	0.29	***0.06***	***0.03***
	67		X	***0.05***	***0.06***	***0.05***	0.76	0.11	***0.01***
	134			X	0.74	***0.01***	***0.03***	0.87	0.61
	202				X	***0.02***	***0.05***	0.65	0.94
No Cover Crop	**0**					X	***0.02***	***0.02***	***0.00***
	67						X	***0.08***	***0.01***
	134							X	0.54
	202								X

C3. N Rate Experiment Oxidative Ratio (cont.)

T-tests (cont.)

Crop Residue

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	**67**	**134**	**202**	**0**	**67**	**134**	**202**
Cover Crop	**0**	X	0.41	0.11	***0.07***	0.82	0.42	0.12	***0.06***
	67		X	***0.06***	***0.05***	0.12	0.93	0.17	***0.02***
	134			X	0.53	***0.02***	***0.05***	0.92	0.41
	202				X	***0.02***	***0.05***	0.69	0.95
No Cover Crop	**0**					X	***0.03***	***0.06***	***0.01***
	67						X	0.16	***0.02***
	134							X	0.62
	202								X

Total Crop

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	**67**	**134**	**202**	**0**	**67**	**134**	**202**
Cover Crop	**0**	X	0.60	0.39	***0.08***	0.80	0.70	0.28	0.13
	67		X	0.54	***0.06***	0.57	0.76	0.37	0.11
	134			X	0.10	0.16	0.26	0.59	0.19
	202				X	***0.04***	***0.05***	0.28	0.53
No Cover Crop	**0**					X	0.71	0.20	***0.05***
	67						X	0.25	***0.06***
	134							X	0.55
	202								X

C3. N Rate Experiment Oxidative Ratio (cont.)

SAS DATA

```
data NRate;
        input Fert Cover$ Organ$ OR;
        cards;
0       Cover       Grain           1.0279
0       Cover       Grain           1.0283
0       Cover       Grain           1.0230
0       Cover       Grain           1.0328
67      Cover       Grain           1.0355
67      Cover       Grain           1.0316
67      Cover       Grain           1.0297
67      Cover       Grain           1.0280
134     Cover       Grain           1.0320
134     Cover       Grain           1.0316
134     Cover       Grain           1.0297
134     Cover       Grain           1.0292
202     Cover       Grain           1.0390
202     Cover       Grain           1.0324
202     Cover       Grain           1.0365
202     Cover       Grain           1.0335
0       NoCover     Grain           1.0302
0       NoCover     Grain           1.0269
0       NoCover     Grain           1.0284
0       NoCover     Grain           1.0312
67      NoCover     Grain           1.0305
67      NoCover     Grain           1.0342
67      NoCover     Grain           1.0303
67      NoCover     Grain           1.0294
134     NoCover     Grain           1.0302
134     NoCover     Grain           1.0300
134     NoCover     Grain           1.0368
134     NoCover     Grain           1.0323
202     NoCover     Grain           1.0325
202     NoCover     Grain           1.0302
202     NoCover     Grain           1.0345
202     NoCover     Grain           1.0357
0       Cover       Reproductive    1.0355
0       Cover       Reproductive    1.0394
0       Cover       Reproductive    1.0335
```

0	Cover	Reproductive	1.0414
67	Cover	Reproductive	1.0338
67	Cover	Reproductive	1.0353
67	Cover	Reproductive	1.0337
67	Cover	Reproductive	1.0368
134	Cover	Reproductive	1.0326
134	Cover	Reproductive	1.0355
134	Cover	Reproductive	1.0319
134	Cover	Reproductive	1.0368
202	Cover	Reproductive	1.0355
202	Cover	Reproductive	1.0384
202	Cover	Reproductive	1.0360
202	Cover	Reproductive	1.0337
0	NoCover	Reproductive	1.0385
0	NoCover	Reproductive	1.0386
0	NoCover	Reproductive	1.0382
0	NoCover	Reproductive	1.0346
67	NoCover	Reproductive	1.0392
67	NoCover	Reproductive	1.0380
67	NoCover	Reproductive	1.0334
67	NoCover	Reproductive	1.0311
134	NoCover	Reproductive	1.0315
134	NoCover	Reproductive	1.0367
134	NoCover	Reproductive	1.0328
134	NoCover	Reproductive	1.0374
202	NoCover	Reproductive	1.0364
202	NoCover	Reproductive	1.0324
202	NoCover	Reproductive	1.0349
202	NoCover	Reproductive	1.0343
0	Cover	LeafStem	1.0349
0	Cover	LeafStem	1.0492
0	Cover	LeafStem	1.0385
0	Cover	LeafStem	1.0406
67	Cover	LeafStem	1.0440
67	Cover	LeafStem	1.0486
67	Cover	LeafStem	1.0442
67	Cover	LeafStem	1.0437
134	Cover	LeafStem	1.0540
134	Cover	LeafStem	1.0488
134	Cover	LeafStem	1.0466
134	Cover	LeafStem	1.0510
202	Cover	LeafStem	1.0570
202	Cover	LeafStem	1.0481

202	Cover	LeafStem	1.0487
202	Cover	LeafStem	1.0503
0	NoCover	LeafStem	1.0408
0	NoCover	LeafStem	1.0407
0	NoCover	LeafStem	1.0421
0	NoCover	LeafStem	1.0433
67	NoCover	LeafStem	1.0448
67	NoCover	LeafStem	1.0438
67	NoCover	LeafStem	1.0437
67	NoCover	LeafStem	1.0469
134	NoCover	LeafStem	1.0440
134	NoCover	LeafStem	1.0508
134	NoCover	LeafStem	1.0515
134	NoCover	LeafStem	1.0527
202	NoCover	LeafStem	1.0500
202	NoCover	LeafStem	1.0484
202	NoCover	LeafStem	1.0543
202	NoCover	LeafStem	1.0525
0	Cover	Residue	1.0350
0	Cover	Residue	1.0472
0	Cover	Residue	1.0374
0	Cover	Residue	1.0408
67	Cover	Residue	1.0418
67	Cover	Residue	1.0454
67	Cover	Residue	1.0415
67	Cover	Residue	1.0420
134	Cover	Residue	1.0480
134	Cover	Residue	1.0455
134	Cover	Residue	1.0430
134	Cover	Residue	1.0473
202	Cover	Residue	1.0519
202	Cover	Residue	1.0457
202	Cover	Residue	1.0456
202	Cover	Residue	1.0458
0	NoCover	Residue	1.0403
0	NoCover	Residue	1.0403
0	NoCover	Residue	1.0413
0	NoCover	Residue	1.0417
67	NoCover	Residue	1.0436
67	NoCover	Residue	1.0425
67	NoCover	Residue	1.0413
67	NoCover	Residue	1.0435
134	NoCover	Residue	1.0407

134	NoCover	Residue	1.0478
134	NoCover	Residue	1.0474
134	NoCover	Residue	1.0492
202	NoCover	Residue	1.0472
202	NoCover	Residue	1.0445
202	NoCover	Residue	1.0495
202	NoCover	Residue	1.0483
0	Cover	Total	1.0323
0	Cover	Total	1.0392
0	Cover	Total	1.0315
0	Cover	Total	1.0380
67	Cover	Total	1.0384
67	Cover	Total	1.0379
67	Cover	Total	1.0350
67	Cover	Total	1.0346
134	Cover	Total	1.0389
134	Cover	Total	1.0374
134	Cover	Total	1.0354
134	Cover	Total	1.0372
202	Cover	Total	1.0446
202	Cover	Total	1.0383
202	Cover	Total	1.0406
202	Cover	Total	1.0387
0	NoCover	Total	1.0358
0	NoCover	Total	1.0346
0	NoCover	Total	1.0356
0	NoCover	Total	1.0373
67	NoCover	Total	1.0364
67	NoCover	Total	1.0378
67	NoCover	Total	1.0352
67	NoCover	Total	1.0359
134	NoCover	Total	1.0349
134	NoCover	Total	1.0374
134	NoCover	Total	1.0415
134	NoCover	Total	1.0396
202	NoCover	Total	1.0391
202	NoCover	Total	1.0364
202	NoCover	Total	1.0412
202	NoCover	Total	1.0414

;

C3. N Rate Experiment Oxidative Ratio (cont.)

SAS CODE

```
proc glm data = NRate;
        class Cover Organ;
        model OR = Fert | Cover| Organ /SS3;
        output out = res r=r1 p=p1;
proc univariate normal plot;
        var r1;
proc plot;
        plot r1*p1;

proc glm data =NRate;
        class Organ;
        model OR = Fert | Organ / SS3;
        output out = res r=r1 p=p1;
proc univariate normal plot;
        var r1;
proc plot;
        plot r1*p1;
run;
```

The SAS System   12:49 Wednesday, October 27, 2010   6

The GLM Procedure

Class Level Information

Class	Levels	Values
Cover	2	Cover NoCover
Organ	5	Grain LeafStem Reproduc Residue Total

Number of Observations Read	160
Number of Observations Used	160

The SAS System   12:49 Wednesday, October 27, 2010   7

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	19	0.00608086	0.00032005	42.80	<.0001
Error	140	0.00104679	0.00000748		
Corrected Total	159	0.00712765			

R-Square	Coeff Var	Root MSE	OR Mean
0.853136	0.263161	0.002734	1.039071

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Fert	1	0.00055483	0.00055483	74.20	<.0001
Cover	1	0.00000743	0.00000743	0.99	0.3204
Fert*Cover	1	0.00000784	0.00000784	1.05	0.3075
Organ	4	0.00119911	0.00029978	40.09	<.0001
Fert*Organ	4	0.00038535	0.00009634	12.88	<.0001
Cover*Organ	4	0.00000164	0.00000041	0.05	0.9943
Fert*Cover*Organ	4	0.00000267	0.00000067	0.09	0.9857

The SAS System 12:49 Wednesday, October 27, 2010 8

The UNIVARIATE Procedure
Variable: r1

Moments

N	160	Sum Weights	160
Mean	0	Sum Observations	0
Std Deviation	0.00256585	Variance	6.5836E-6
Skewness	0.32310506	Kurtosis	0.02498108
Uncorrected SS	0.00104679	Corrected SS	0.00104679
Coeff Variation	.	Std Error Mean	0.00020285

Basic Statistical Measures

Location		Variability	
Mean	0.00000	Std Deviation	0.00257
Median	-0.00039	Variance	6.5836E-6
Mode	-0.00058	Range	0.01430
		Interquartile Range	0.00364

Tests for Location: Mu0=0

Test	-Statistic-	-----p Value------

Student's t	t	0	Pr > |t|	1.0000
Sign	M	-4	Pr >= |M|	0.5801
Signed Rank	S	-253	Pr >= |S|	0.6678

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.990362	Pr < W	0.3495
Kolmogorov-Smirnov	D	0.067666	Pr > D	0.0732
Cramer-von Mises	W-Sq	0.09264	Pr > W-Sq	0.1426
Anderson-Darling	A-Sq	0.534193	Pr > A-Sq	0.1767

Quantiles (Definition 5)

Quantile	Estimate
100% Max	0.007769508
99%	0.006905590
95%	0.004700195
90%	0.003500813
75% Q3	0.001722750
50% Median	-0.000393514
25% Q1	-0.001914071
10%	-0.003118498

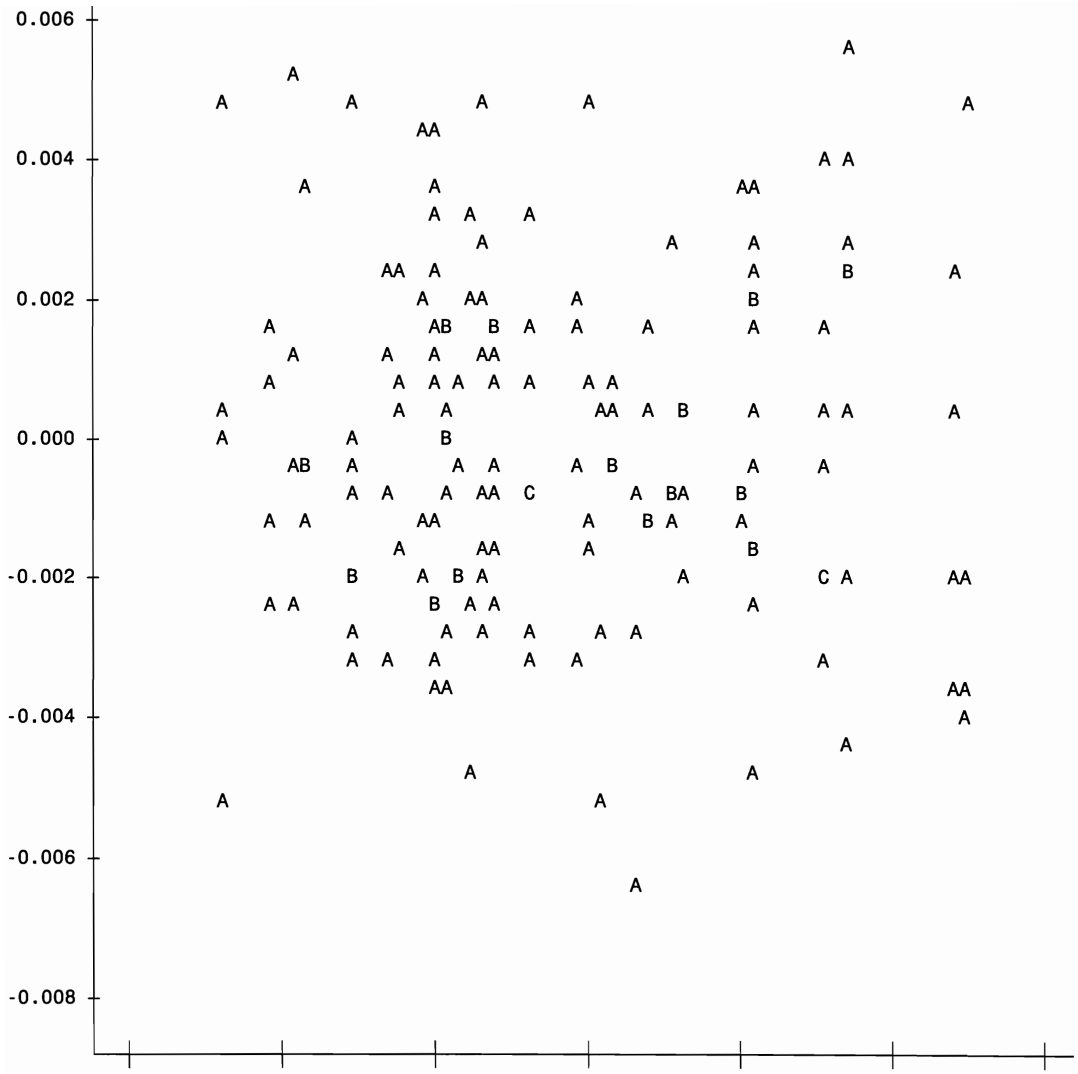
The UNIVARIATE Procedure
Variable: r1

Quantiles (Definition 5)

Quantile	Estimate

```
              5%              -0.003538020
              1%              -0.005294410
              0% Min          -0.006530492


                 Extreme Observations

   -------Lowest-------        -------Highest------

         Value      Obs              Value      Obs

   -0.00653049       65         0.00499145       36
   -0.00529441       97         0.00528442        5
   -0.00507521        3         0.00547781       73
   -0.00488825       56         0.00690559       98
   -0.00475326      121         0.00776951       66


Stem Leaf                       #             Boxplot
   7 8                          1                0
   6 9                          1                |
   5 035                        3                |
   4 12357779                   8                |
   3 01234667                   8                |
   2 0012233445689             13                |
   1 00224444556777778999      20             +-----+
   0 1222233333445557777899    22             |  +  |
  -0 9998888887666655444432    22             *-----*
  -1 9999986665544332211100000 25             +-----+
  -2 99987766642222111100      20                |
  -3 6544433321                10                |
  -4 9860                       4                |
  -5 31                         2                |
  -6 5                          1                |
     ----+----+----+----+----+
 Multiply Stem.Leaf by 10**-3
```

```
                    The SAS System       12:49 Wednesday, October 27, 2010  10

                The UNIVARIATE Procedure
                    Variable:  r1

                    Normal Probability Plot
    0.0075+                                                 *
          |                                              *++
          |                                           **++
          |                                      ******
          |                                    ***+
          |                                ****
          |                            *****
    0.0005+                        +****
          |                     *****
          |                 ****
          |            *****
          |       *****+
          |    ****+
          | *+*+
   -0.0065+*+
           +----+----+----+----+----+----+----+----+----+----+
               -2        -1         0        +1        +2


                    The SAS System       12:49 Wednesday, October 27, 2010  11

          Plot of r1*p1.  Legend: A = 1 obs, B = 2 obs, etc.

 r1 |
    |
0.008 +
    |                                         A
    |
    |                                      A
    |
```


0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008

1.025 1.030 1.035 1.040 1.045 1.050 1.055

p1

The SAS System 12:49 Wednesday, October 27, 2010 12

The GLM Procedure

Class Level Information

Class	Levels	Values
Organ	5	Grain LeafStem Reproduc Residue Total

Number of Observations Read	160
Number of Observations Used	160

The SAS System 12:49 Wednesday, October 27, 2010 13

The GLM Procedure

Dependent Variable: OR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	9	0.00606891	0.00067432	95.54	<.0001
Error	150	0.00105874	0.00000706		
Corrected Total	159	0.00712765			

R-Square	Coeff Var	Root MSE	OR Mean
0.851461	0.255684	0.002657	1.039071

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Fert	1	0.00055483	0.00055483	78.61	<.0001
Organ	4	0.00119911	0.00029978	42.47	<.0001
Fert*Organ	4	0.00038535	0.00009634	13.65	<.0001

The UNIVARIATE Procedure
Variable: r1

Moments

N	160	Sum Weights	160
Mean	0	Sum Observations	0
Std Deviation	0.00258045	Variance	6.65872E-6
Skewness	0.22135083	Kurtosis	-0.0330263
Uncorrected SS	0.00105874	Corrected SS	0.00105874
Coeff Variation	.	Std Error Mean	0.000204

Basic Statistical Measures

Location		Variability	
Mean	0.00000	Std Deviation	0.00258
Median	-0.00029	Variance	6.65872E-6
Mode	-0.00139	Range	0.01430
		Interquartile Range	0.00364

Note: The mode displayed is the smallest of 3 modes with a count of 2.

Tests for Location: Mu0=0

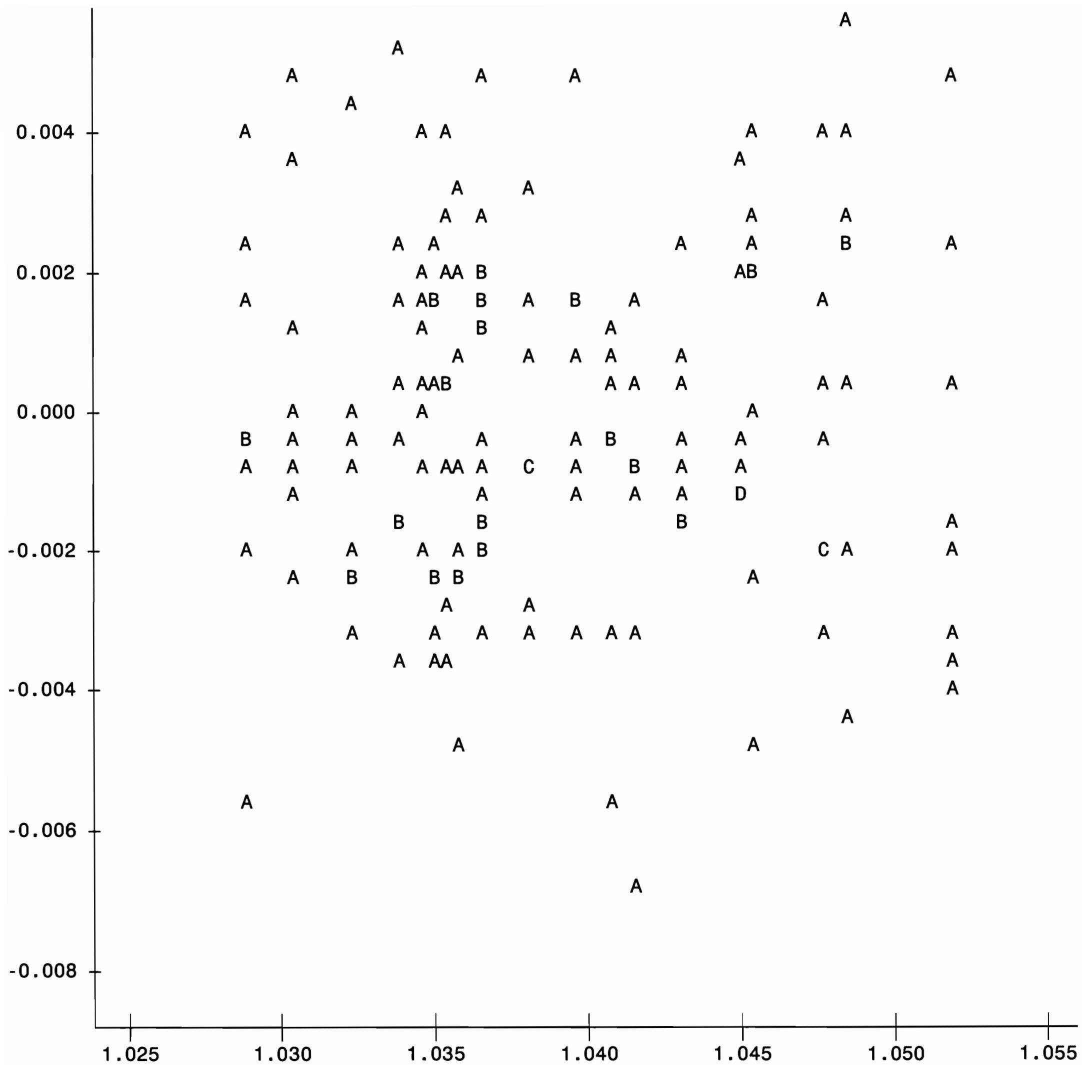
Test -Statistic- -----p Value------

```
          Student's t    t         0    Pr > |t|    1.0000
          Sign           M        -6    Pr >= |M|   0.3846
          Signed Rank    S      -151    Pr >= |S|   0.7979


                       Tests for Normality

Test                  --Statistic---    -----p Value------

Shapiro-Wilk          W     0.993641    Pr < W      0.7120
Kolmogorov-Smirnov    D     0.056896    Pr > D     >0.1500
Cramer-von Mises      W-Sq  0.064923    Pr > W-Sq  >0.2500
Anderson-Darling      A-Sq  0.379475    Pr > A-Sq  >0.2500


                Quantiles (Definition 5)

                Quantile         Estimate

                100% Max       0.00755703
                99%            0.00661224
                95%            0.00464032
                90%            0.00360406
                75% Q3         0.00173778
                50% Median    -0.00028946

                      The SAS System       12:49 Wednesday, October 27, 2010  15

                 The UNIVARIATE Procedure
                      Variable:  r1

                Quantiles (Definition 5)

                Quantile         Estimate

                25% Q1        -0.00190224
                10%           -0.00321510
                5%            -0.00375408
```

```
            1%              -0.00576513
            0% Min          -0.00674297


                Extreme Observations

   -------Lowest-------       -------Highest------

         Value      Obs             Value      Obs

   -0.00674297       65        0.00499927        5
   -0.00576513        3        0.00500218       13
   -0.00558776       97        0.00546064       73
   -0.00483371       56        0.00661224       98
   -0.00463394      121        0.00755703       66


Stem Leaf                           #             Boxplot
   7 6                              1                0
   6 6                              1                |
   5 0005                           4                |
   4 00022679                       8                |
   3 033579                         6                |
   2 0011123344555778              16                |
   1 11112445556677778889          20             +-----+
   0 122334555556667799            18             |  +  |
  -0 99988888766665555433332210    26             *-----*
  -1 9997776555444322110000        22             +-----+
  -2 986555432211110000            18                |
  -3 98776333322210                14                |
  -4 865                            3                |
  -5 86                             2                |
  -6 7                              1                |
     ----+----+----+----+----+-
 Multiply Stem.Leaf by 10**-3
```

```
                    The SAS System       12:49 Wednesday, October 27, 2010  16

                The UNIVARIATE Procedure
                    Variable:  r1

                    Normal Probability Plot
  0.0075+                                                 *
        |                                               *++
        |                                            **++
        |                                       *****
        |                                    ***+
        |                                *****
        |                            *****
  0.0005+                        +****
        |                    ******
        |                 ****
        |             *****
        |       ******
        |    ***++
        | *+*+
-0.0065+*+
         +----+----+----+----+----+----+----+----+----+----+
             -2        -1         0        +1        +2
```

```
                    The SAS System       12:49 Wednesday, October 27, 2010  17

        Plot of r1*p1.  Legend: A = 1 obs, B = 2 obs, etc.

  r1 |
     |
0.008 +
     |                                  A
     |
     |                                A
     |
0.006 +
```


0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
1.025
1.030
1.035
1.040
1.045
1.050
1.055

C4. N Rate Experiment Biochemical Stocks without a Cover Crop

T-tests

Crop Organs

Carbohydrate

Fertilization Rate (kg N ha-1)		Grain				Reproductive Support				Leaf & Stem			
		0	67	134	202	0	67	134	202	0	67	134	202
Grain	0	X	0.0002	0.0000	0.0000	0.0007	0.0011	0.0004	0.0007	0.4235	0.8710	0.8736	0.2131
	67		X	0.0341	0.0034	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000
	134			X	0.1892	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001	0.0000	0.0001
	202				X	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Rep Support	0					X	0.0051	0.0208	0.0025	0.0012	0.0000	0.0001	0.0000
	67						X	0.2414	0.0404	0.0019	0.0000	0.0003	0.0000
	134							X	0.4525	0.0010	0.0000	0.0000	0.0000
	202								X	0.0016	0.0000	0.0001	0.0000
Leaf & Stem	0									X	0.3964	0.3003	0.0721
	67										X	0.6274	0.0082
	134											X	0.1306
	202												X

Protein

Fertilization Rate (kg N ha-1)		Grain				Reproductive Support				Leaf & Stem			
		0	67	134	202	0	67	134	202	0	67	134	202
Grain	0	X	0.00105	0.0001	0.0000	0.0022	0.0027	0.0027	0.0027	0.0048	0.1149	0.6703	0.0376
	67		X	0.0444	0.0019	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0019	0.0003
	134			X	0.3633	0.0003	0.0003	0.0003	0.0003	0.0000	0.0002	0.0001	0.0007
	202				X	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000
Rep Support	0					X	0.0943	0.0122	0.0192	0.0104	0.0004	0.0026	0.0001
	67						X	0.0695	0.1358	0.0149	0.0007	0.0031	0.0002
	134							X	0.5311	0.0202	0.0004	0.0032	0.0001
	202								X	0.0180	0.0005	0.0032	0.0001
Leaf & Stem	0									X	0.0083	0.0049	0.0001
	67										X	0.0774	0.0004
	134											X	0.0989
	202												X

C4. N Rate Experiment Biochemical Stocks without a Cover Crop (cont.)

Crop Organs (cont.)

Lignin

Fertilization Rate (kg N ha-1)		Grain				Reproductive Support				Leaf & Stem			
		0	67	134	202	0	67	134	202	0	67	134	202
Grain	0	X	0.0144	0.0010	0.0006	0.0784	0.2815	0.4953	0.0386	0.0030	0.0000	0.0001	0.0000
	67		X	0.5152	0.1031	0.0046	0.0380	0.0323	0.1834	0.0048	0.0000	0.0000	0.0000
	134			X	0.1139	0.0000	0.0005	0.0063	0.0228	0.0090	0.0002	0.0004	0.0000
	202				X	0.0002	0.0035	0.0015	0.0059	0.0104	0.0000	0.0001	0.0000
Rep Support	0					X	0.0086	0.0467	0.0035	0.0027	0.0000	0.0001	0.0000
	67						X	0.9113	0.0948	0.0047	0.0002	0.0003	0.0001
	134							X	0.1500	0.0028	0.0000	0.0000	0.0000
	202								X	0.0044	0.0000	0.0001	0.0000
Leaf & Stem	0									X	0.2940	0.1317	0.0276
	67										X	0.3153	0.0062
	134											X	0.0564
	202												X

Lipid

Fertilization Rate (kg N ha-1)		Grain				Reproductive Support				Leaf & Stem			
		0	67	134	202	0	67	134	202	0	67	134	202
Grain	0	X	0.0181	0.0475	0.0038	0.0438	0.0322	0.0406	0.0360	0.0460	0.0117	0.0305	0.0108
	67		X	0.6188	0.2079	0.0058	0.0041	0.0056	0.0042	0.5196	0.6343	0.5566	0.3113
	134			X	0.6442	0.0195	0.0172	0.0190	0.0177	0.3567	0.4198	0.9713	0.7366
	202				X	0.0030	0.0020	0.0029	0.0020	0.0820	0.0824	0.6442	0.8955
Rep Support	0					X	0.6176	0.8008	0.8289	0.0090	0.0009	0.0133	0.0064
	67						X	0.7501	0.8188	0.0065	0.0003	0.0113	0.0051
	134							X	0.9689	0.0086	0.0008	0.0129	0.0062
	202								X	0.0067	0.0003	0.0116	0.0052
Leaf & Stem	0									X	0.7566	0.2961	0.1416
	67										X	0.3490	0.1615
	134											X	0.7470
	202												X

C4. N Rate Experiment Biochemical Stocks without a Cover Crop (cont.)

Grain versus Crop Residue

Carbohydrate

Fertilization Rate (kg N ha^{-1})		Grain				Residue			
		0	67	134	202	0	67	134	202
Grain	0	X	0.00022	0.00001	0.00001	0.13946	0.01396	0.00543	0.00182
	67		X	0.03408	0.00335	0.00137	0.00000	0.00130	0.00003
	134			X	0.18916	0.00011	0.00047	0.00012	0.00039
	202				X	0.00009	0.00013	0.00005	0.00005
Residue	0					X	0.17850	0.09274	0.02137
	67						X	0.37714	0.00362
	134							X	0.16005
	202								X

Protein

Fertilization Rate (kg N ha^{-1})		Grain				Residue			
		0	67	134	202	0	67	134	202
Grain	0	X	0.00105	0.00009	0.00002	0.01526	0.64797	0.13483	0.00666
	67		X	0.04438	0.00188	0.00016	0.00011	0.00485	0.00194
	134			X	0.36330	0.00004	0.00023	0.00031	0.00098
	202				X	0.00000	0.00000	0.00024	0.00001
Residue	0					X	0.00978	0.00450	0.00011
	67						X	0.06787	0.00090
	134							X	0.14931
	202								X

C4. N Rate Experiment Biochemical Stocks without a Cover Crop (cont.)

Grain versus Crop Residue (cont.)

Lignin

Fertilization Rate (kg N ha^{-1})		Grain				Residue			
		0	67	134	202	0	67	134	202
Grain	0	X	0.01435	0.00103	0.00057	0.00153	0.00000	0.00012	0.00002
	67		X	0.51524	0.10311	0.00184	0.00000	0.00006	0.00001
	134			X	0.11386	0.00383	0.00006	0.00041	0.00010
	202				X	0.00366	0.00001	0.00018	0.00002
Residue	0					X	0.11019	0.05920	0.00744
	67						X	0.43942	0.00890
	134							X	0.05427
	202								X

Lipid

Fertilization Rate (kg N ha^{-1})		Grain				Residue			
0	0	0	67	134	202	0	67	134	202
Grain	0	X	0.01812	0.04753	0.00379	0.00678	0.00507	0.01264	0.01132
	67		X	0.61876	0.20791	0.75597	0.59562	0.22272	0.15223
	134			X	0.64424	0.75541	0.81333	0.55778	0.40840
	202				X	0.27195	0.26677	0.82531	0.59033
Residue	0					X	0.84375	0.28469	0.19305
	67						X	0.29964	0.20626
	134							X	0.76959
	202								X

C4. N Rate Experiment Biochemical Stocks without a Cover Crop (cont.)

Total Plant

Carbohydrate

Fertilization Rate (kg N ha^{-1})		Total Plant			
		0	67	134	202
Total Plant	0	X	0.00381	0.00037	0.00038
	67		X	0.07979	0.00233
	134			X	0.11982
	202				X

Protein

Fertilization Rate (kg N ha^{-1})		Total Plant			
		0	67	134	202
Total Plant	0	X	0.00134	0.00044	0.00003
	67		X	0.05049	0.00074
	134			X	0.22766
	202				X

Lignin

Fertilization Rate (kg N ha^{-1})		Total Plant			
		0	67	134	202
Total Plant	0	X	0.03972	0.01607	0.00240
	67		X	0.32180	0.00637
	134			X	0.03780
	202				X

Lipid

Fertilization Rate (kg N ha^{-1})		Total Plant			
0	0	0	67	134	202
Total Plant	0	X	0.06240	0.09930	0.02336
	67		X	0.42898	0.14638
	134			X	0.68931
	202				X

C5. N Rate Experiment Cost Assessment

T-tests

Cost per Total Mass Yield ($ Mg^{-1})

Fertilization Rate (kg N ha^{-1})		Cover Crop							No Cover Crop						
		0	34	67	101	134	168	202	0	34	67	101	134	168	202
Cover Crop	0	X	0.007	0.001	0.003	0.003	0.004	0.003	0.010	0.003	0.003	0.002	0.002	0.001	0.003
	34		X	0.029	0.006	0.002	0.004	0.102	0.610	0.058	0.002	0.001	0.003	0.033	0.003
	67			X	0.889	0.514	0.788	0.297	0.077	0.312	0.180	0.269	0.420	0.940	0.702
	101				X	0.208	0.472	0.241	0.084	0.229	0.032	0.084	0.219	0.824	0.400
	134					X	0.349	0.069	0.054	0.049	0.073	0.363	0.721	0.601	0.579
	168						X	0.122	0.069	0.095	0.005	0.135	0.371	0.877	0.777
	202							X	0.186	0.904	0.029	0.033	0.061	0.285	0.103
No Cover Crop	0								X	0.167	0.037	0.038	0.043	0.073	0.063
	34									X	0.018	0.022	0.052	0.300	0.079
	67										X	0.631	0.428	0.229	0.041
	101											X	0.707	0.332	0.205
	134												X	0.491	0.481
	168													X	0.790
	202														X

Cost per Grain Mass Yield ($ Mg^{-1})

Fertilization Rate (kg N ha^{-1})		Cover Crop							No Cover Crop						
		0	34	67	101	134	168	202	0	34	67	101	134	168	202
Cover Crop	0	X	0.014	0.006	0.007	0.006	0.007	0.007	0.025	0.009	0.006	0.006	0.006	0.006	0.007
	34		X	0.009	0.001	0.000	0.002	0.006	0.059	0.038	0.000	0.000	0.000	0.003	0.000
	67			X	0.713	0.235	0.561	0.649	0.005	0.138	0.174	0.141	0.227	0.653	0.530
	101				X	0.077	0.614	0.295	0.008	0.036	0.034	0.035	0.122	0.841	0.593
	134					X	0.056	0.067	0.006	0.013	0.489	0.374	0.899	0.417	0.178
	168						X	0.202	0.009	0.034	0.011	0.043	0.160	0.982	0.851
	202							X	0.007	0.200	0.049	0.036	0.064	0.334	0.189
No Cover Crop	0								X	0.014	0.006	0.005	0.005	0.004	0.007
	34									X	0.011	0.007	0.010	0.055	0.025
	67										X	0.680	0.728	0.295	0.075
	101											X	0.544	0.238	0.072
	134												X	0.404	0.238
	168													X	0.919
	202														X

C5. N Rate Experiment Cost Assessment (cont.)

Cropping for Grain Protein ($ Mg^{-1})

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	67	134	202	0	67	134	202
Cover Crop	0	X	**0.000**	**0.000**	**0.000**	**0.018**	**0.000**	**0.000**	**0.000**
	67		X	0.037	0.099	0.019	0.205	0.100	0.159
	134			X	0.240	0.008	0.082	0.286	0.112
	202				X	0.014	0.013	0.976	0.182
No Cover Crop	0					X	**0.017**	**0.012**	**0.015**
	67						X	0.267	0.443
	134							X	0.464
	202								X

Cropping for Grain Carbohydrate ($ Mg^{-1})

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	67	134	202	0	67	134	202
Cover Crop	0	X	**0.009**	**0.009**	**0.011**	**0.038**	0.009	0.009	0.010
	67		X	0.260	0.418	0.005	0.199	0.282	0.711
	134			X	**0.040**	0.006	0.650	0.930	0.137
	202				X	0.009	0.035	0.043	0.148
No Cover Crop	0					X	**0.007**	**0.005**	**0.008**
	67						X	0.620	0.052
	134							X	0.190
	202								X

Cropping for Grain Carbohydrate ($ Mg^{-1})

Fertilization Rate (kg N ha^{-1})		Cover Crop				No Cover Crop			
		0	67	134	202	0	67	134	202
Cover Crop	0	X	**0.003**	**0.002**	**0.001**	**0.050**	0.006	0.001	0.002
	67		X	0.055	**0.042**	0.185	0.813	0.410	0.006
	134			X	0.641	0.068	0.029	0.662	0.065
	202				X	0.055	0.037	0.500	0.218
No Cover Crop	0					X	0.167	0.101	**0.036**
	67						X	0.450	**0.002**
	134							X	0.190
	202								X

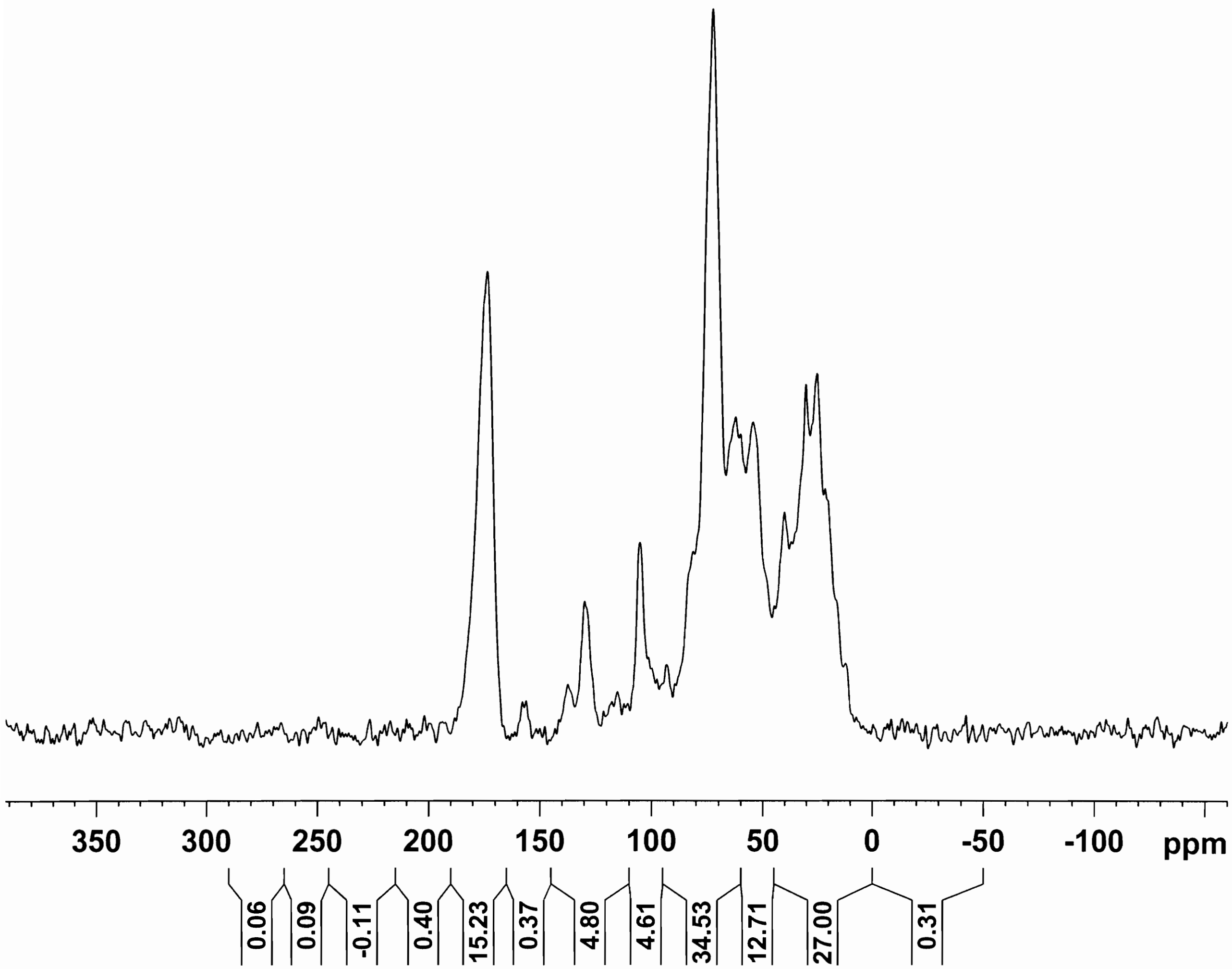
APPENDIX D

^{13}C NMR Cross Polarization Spectra

Solid-state ^{13}C NMR was performed at Rice University using Bruker 200 MHz NMR spectrometer. C-13 NMR cross polarization-magic angle spinning spectra were collected for grain and stover samples from the Kellogg Biological Station – Long Term Ecological Research Treatment 1 Crops (Figure D1) and grain, leaf and stem, and reproductive support samples from the N Rate Experiment (Figure D2).

Figure D1. KBS-LTER Treatment 1 Crops

Kellogg Biological Station Long Term Ecological Research Station
2003 Treatment 1 Replicate 1 Soybean Grain (GLYGR)
03/19/2010   106.8 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

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EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1258
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	294.2 K
D1	3.00000000 sec
TD0	20

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.20 dB
SFO1	50.3287070 MHz

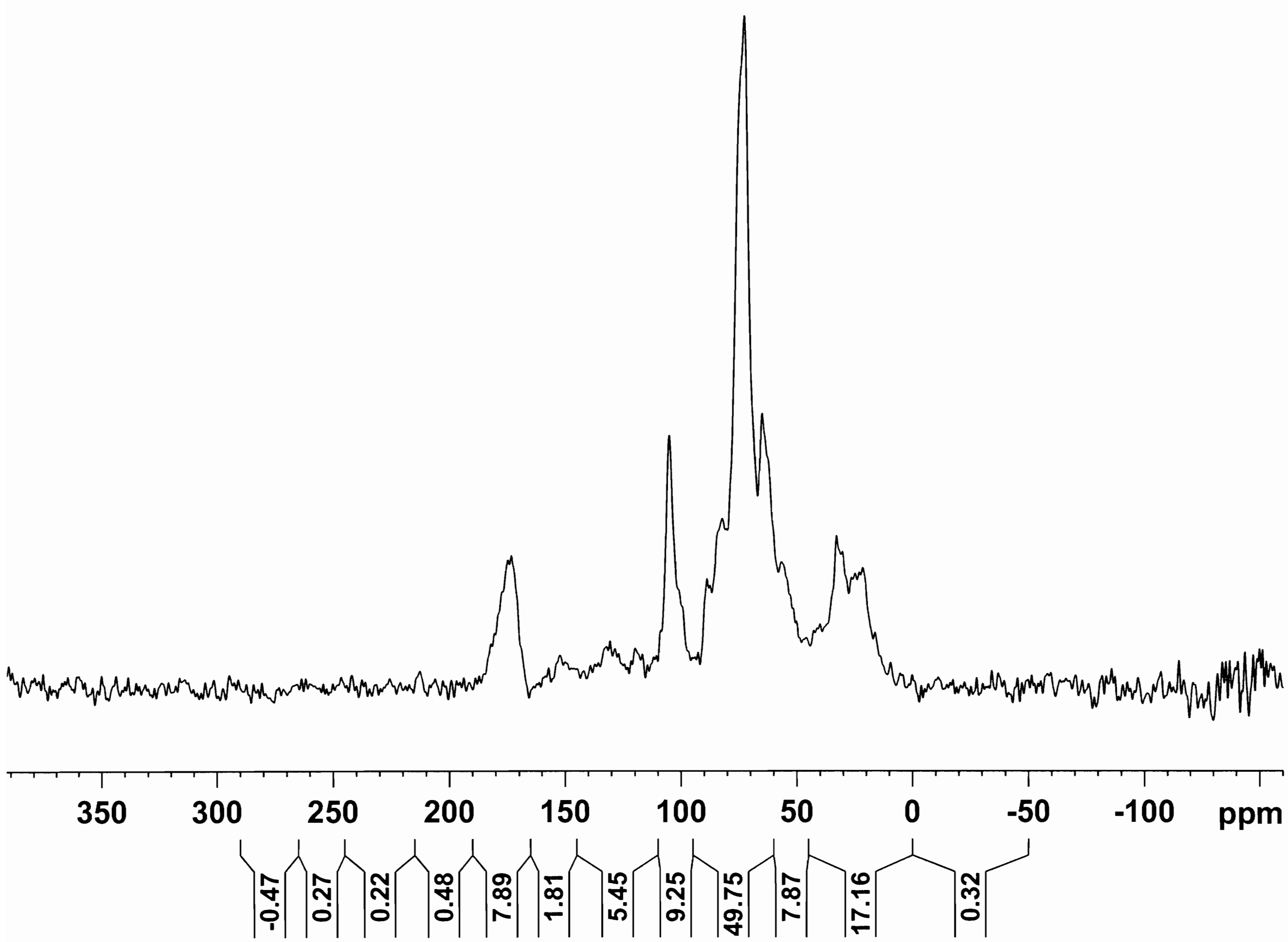
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.10 usec
P31	5.60 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228798 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Kellogg Biological Station Long Term Ecological Research Station
2003 Treatment 1 Replicate 1 Soybean Stover (GLYST)
04/21/2010   85.2 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

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PROCNO                     1

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SOLVENT
NS                  1200
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FIDRES         27.126736 Hz
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RG                  2048
DW                18.000 usec
DE                 17.00 usec
TE                 293.2 K
D1            3.00000000 sec
TD0                   12

======== CHANNEL f1 ========
NUC1                 13C
P15              1000.00 usec
PL1                 2.20 dB
SFO1          50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2           tppm15
NUC2                  1H
P3                  3.10 usec
P31                 5.80 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3228757 MHz
WDW                   EM
SSB                    0
LB                 30.00 Hz
GB                     0
PC                  1.00
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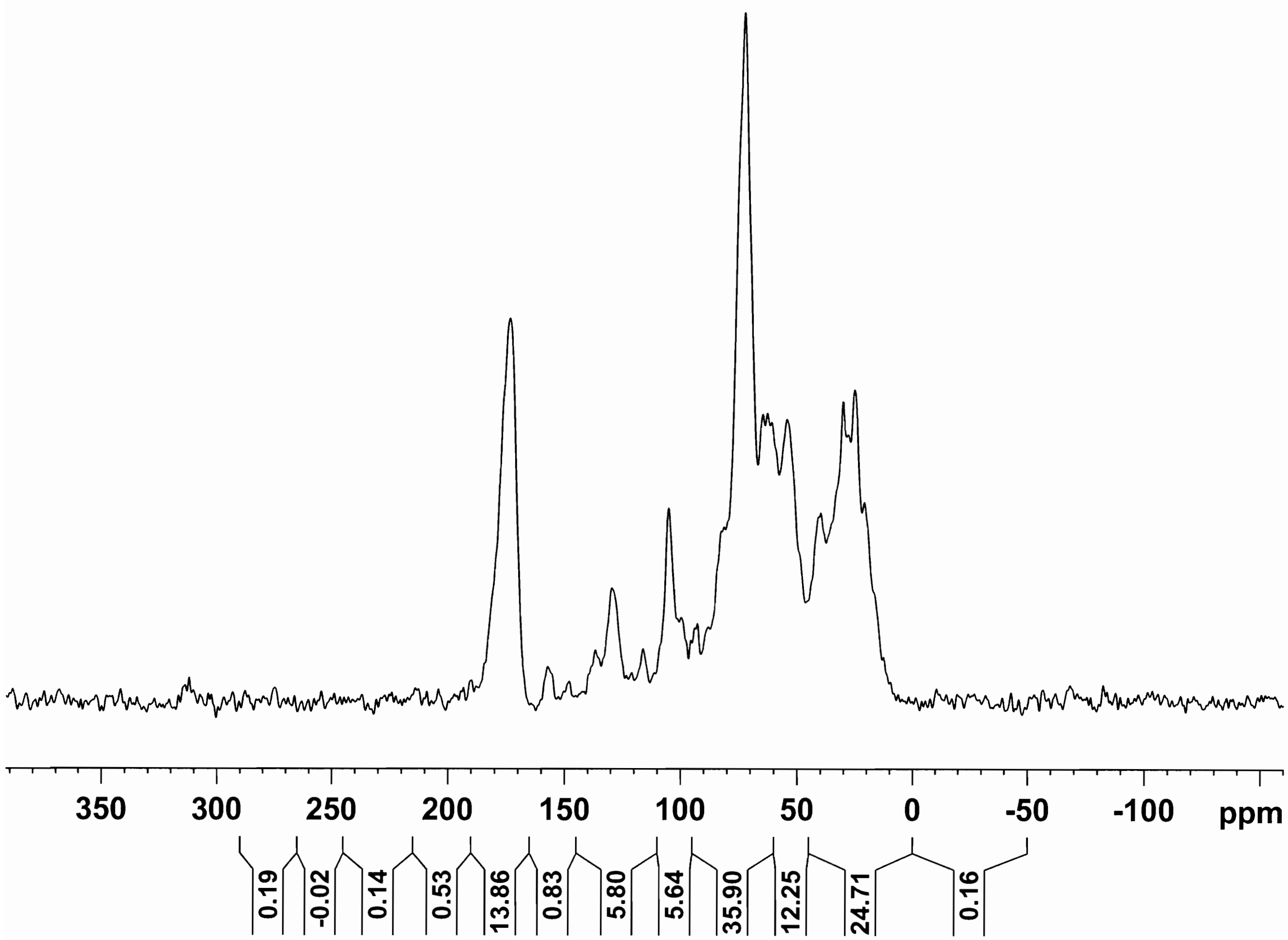
Kellogg Biological Station Long Term Ecological Research Station
2003 Treatment 1 Replicate 2 Soybean Grain (GLYGR)
03/21/2010   115.6 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.

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PROCNO                     1

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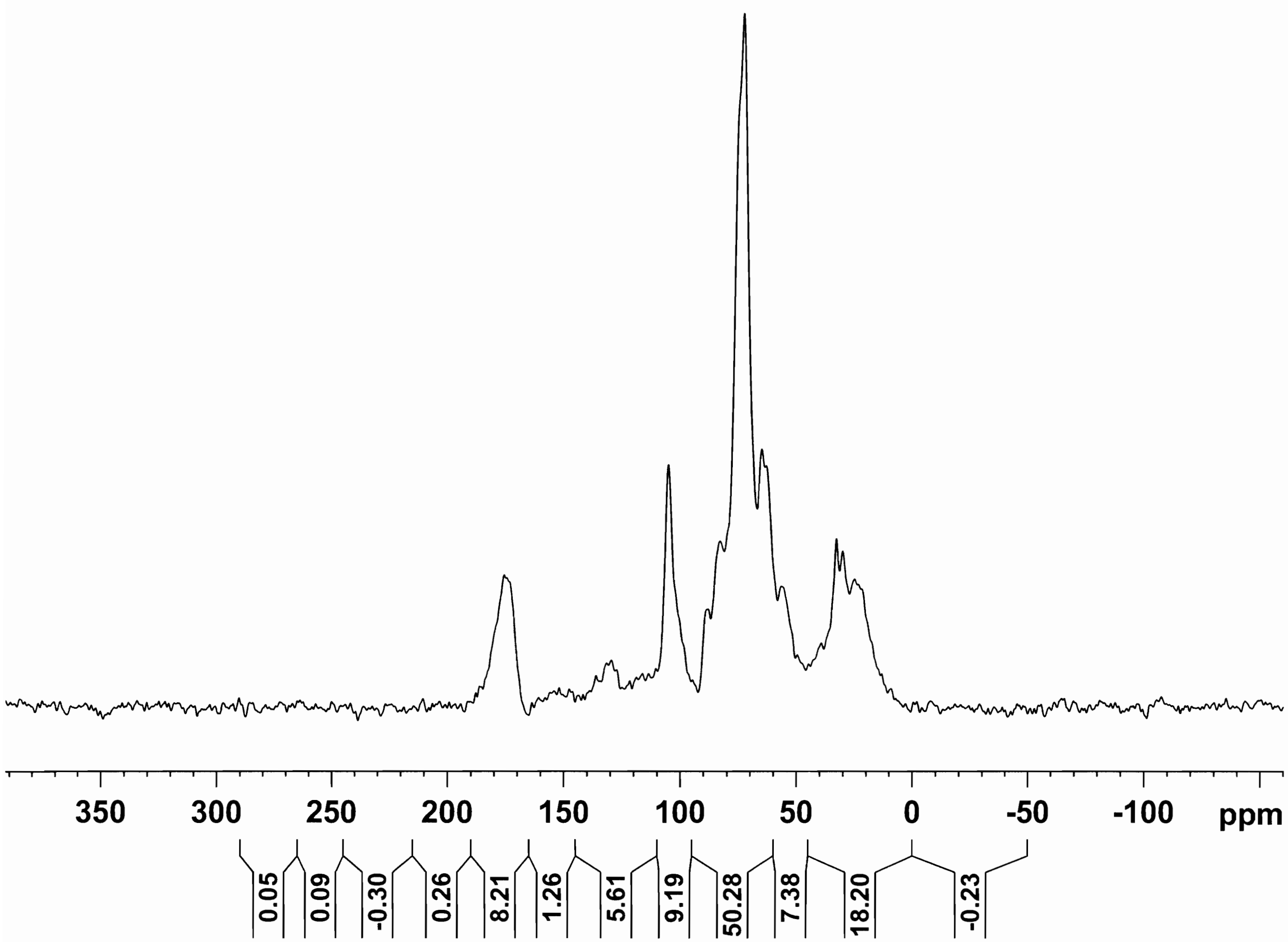
PULPROG           cp.99.WCH
TD                      1024
SOLVENT
NS                      1110
DS                         0
SWH               27777.777 Hz
FIDRES            27.126736 Hz
AQ                0.0185000 sec
RG                      2048
DW                    18.000 usec
DE                     17.00 usec
TE                     294.1 K
D1                3.00000000 sec
TD0                       20

======== CHANNEL f1 ========
NUC1                     13C
P15                  1000.00 usec
PL1                     2.20 dB
SFO1              50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                      3.10 usec
P31                     5.60 usec
PL2                     6.00 dB
PL12                    3.00 dB
SFO2             200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF                50.3228798 MHz
WDW                       EM
SSB                        0
LB                     40.00 Hz
GB                         0
PC                      1.00
```

Kellogg Biological Station Long Term Ecological Research Station
2003 Treatment 1 Replicate 2 Soybean Stover (GLYST)
03/19/2010   89.3 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

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PROCNO   1

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TD   1024
SOLVENT
NS   2000
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   294.2 K
D1   3.00000000 sec
TD0   20

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.20 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.10 usec
P31   5.60 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228798 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Kellogg Biological Station Long Term Ecological Research Station
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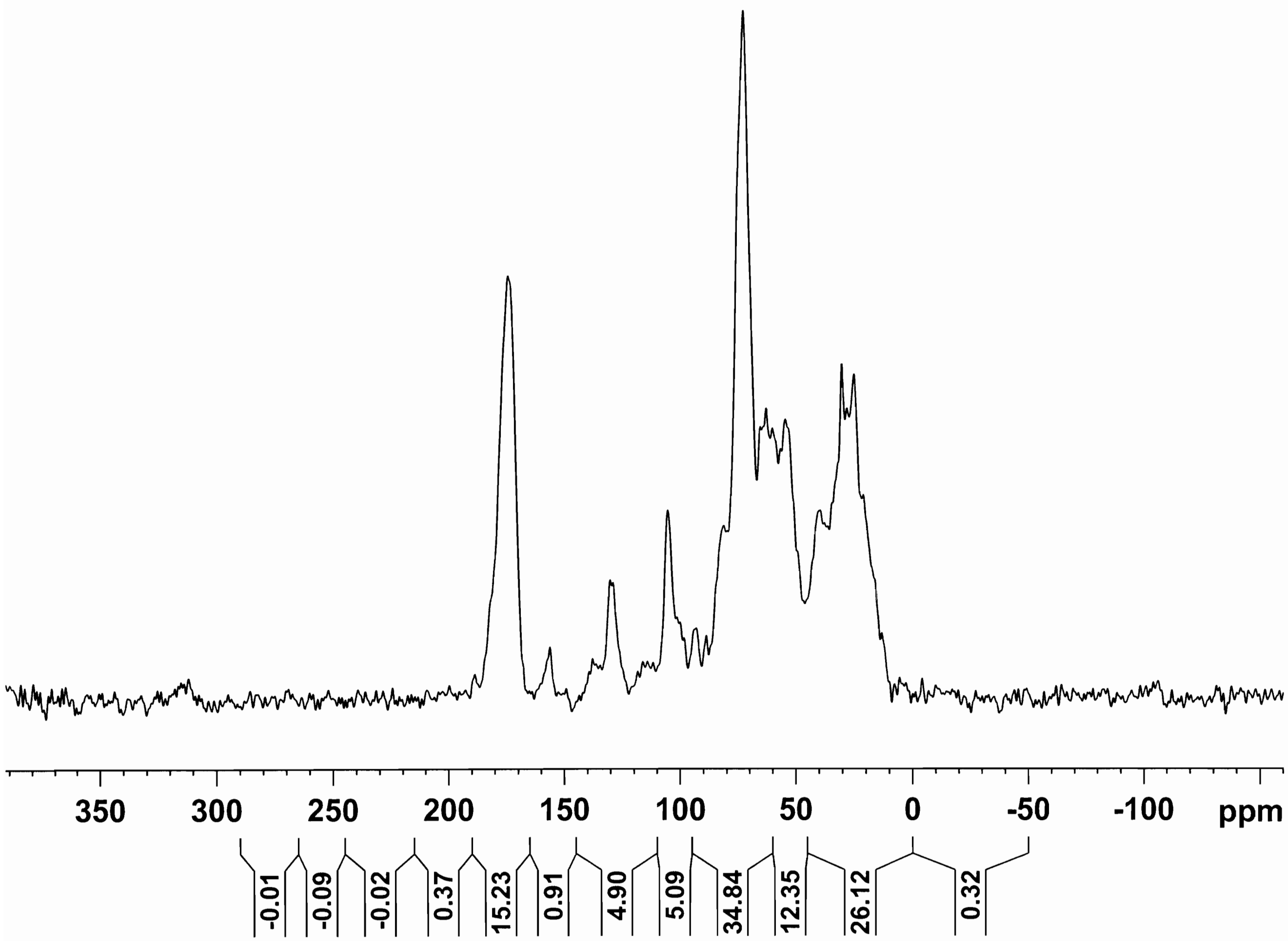
04/21/2010 109.3 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

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PROCNO 1

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INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1200
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 293.1 K
D1 3.00000000 sec
TD0 12

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.20 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.80 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228757 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Kellogg Biological Station Long Term Ecological Research Station
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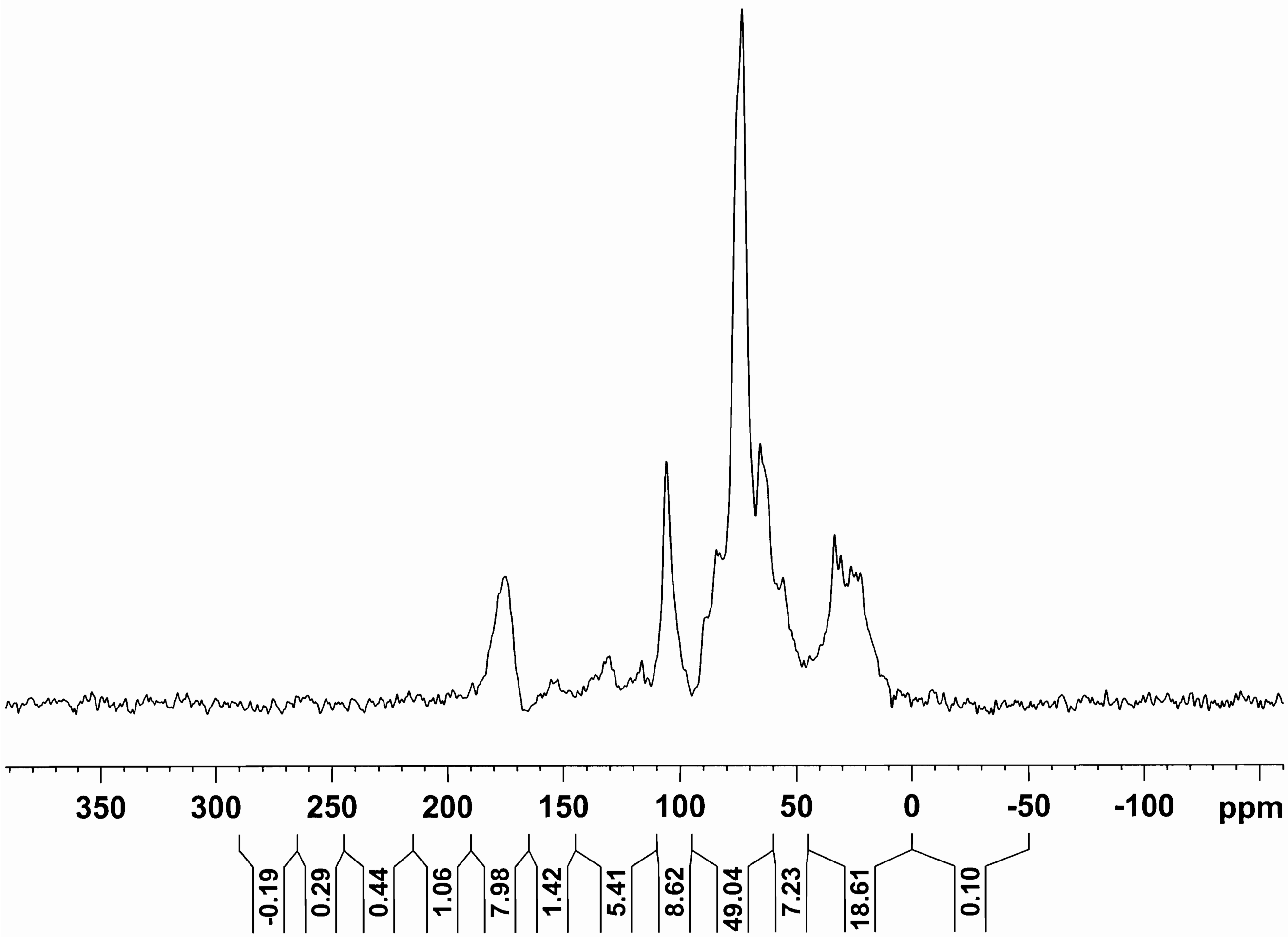
03/21/2010   81.5 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



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PROCNO   1

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TD   1024
SOLVENT
NS   1609
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
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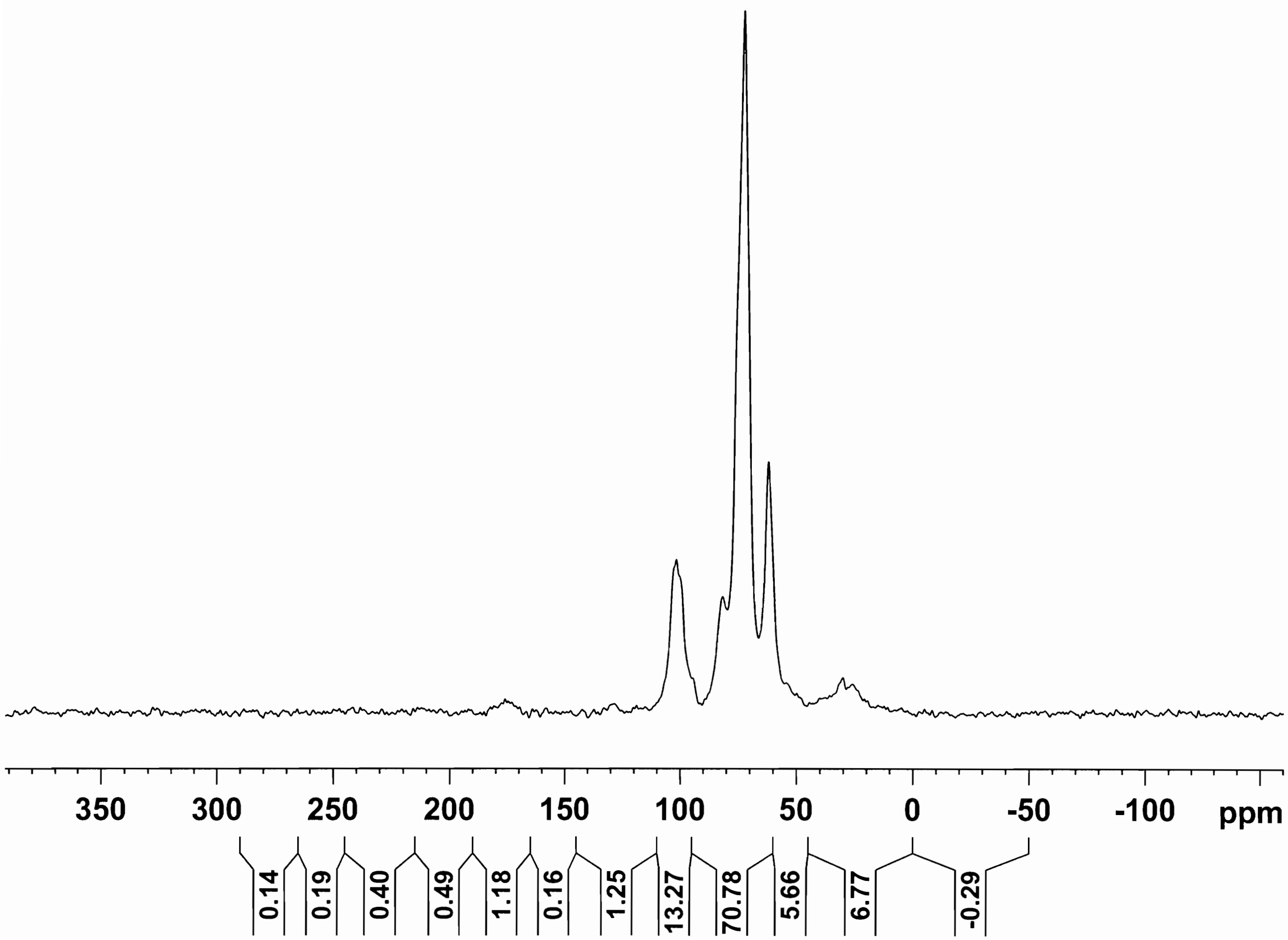
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   294.0 K
D1   3.00000000 sec
TD0   20

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.20 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.10 usec
P31   5.60 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228798 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 1 Wheat Grain (TRIGR)
03/18/2010   107.9 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBS 2004 T1R1 TRIGR
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters

Date_	20100318	
Time	19.35	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1066	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	294.2	K
D1	3.00000000	sec
TD0	20	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.20	dB
SFO1	50.3287070	MHz

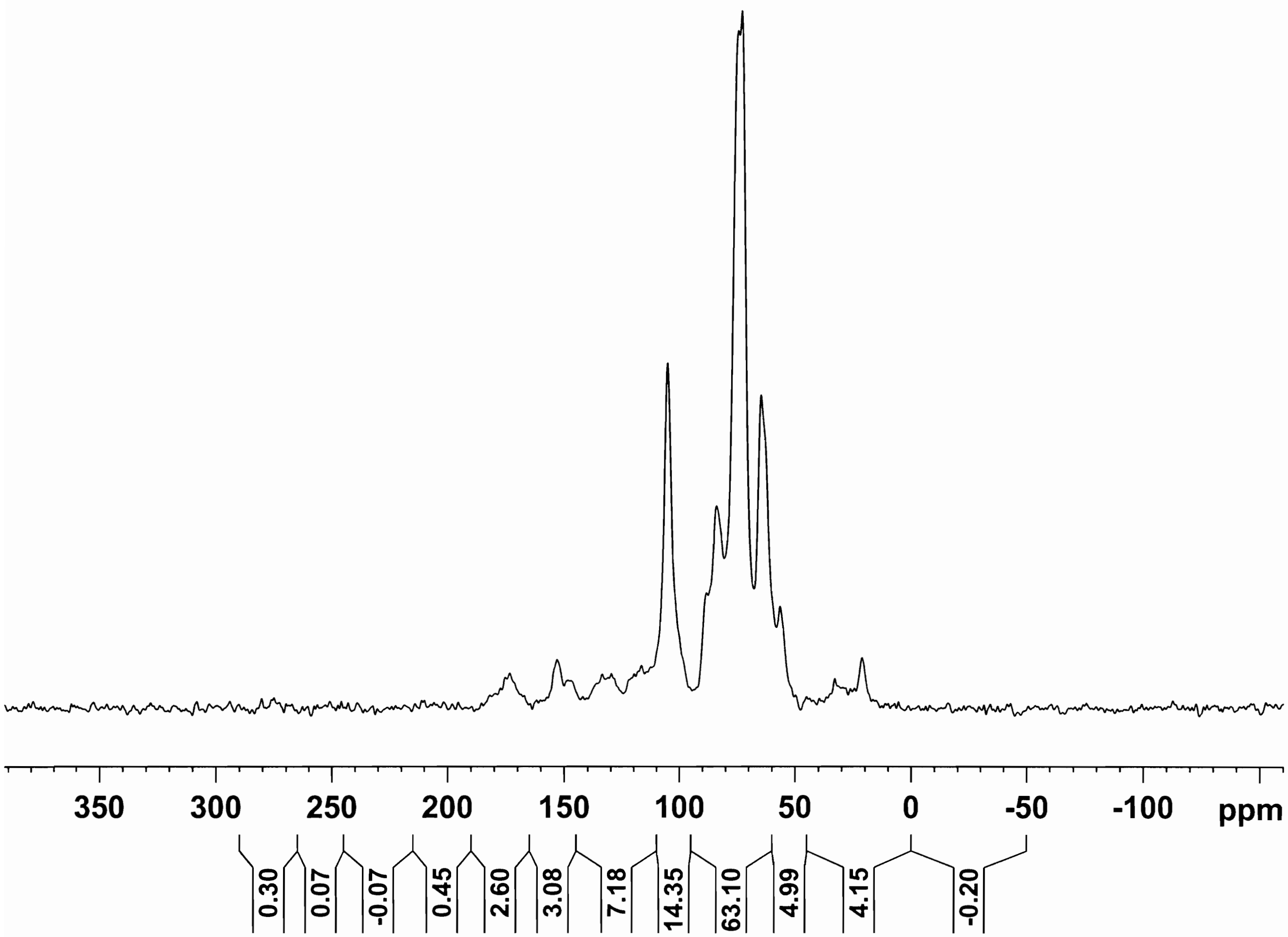
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.60	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228798	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 1 Wheat Stover (TRIST)
03/18/2010 65.4 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBS 2004 T1R1 TRIST
EXPNO 1
PROCNO 1

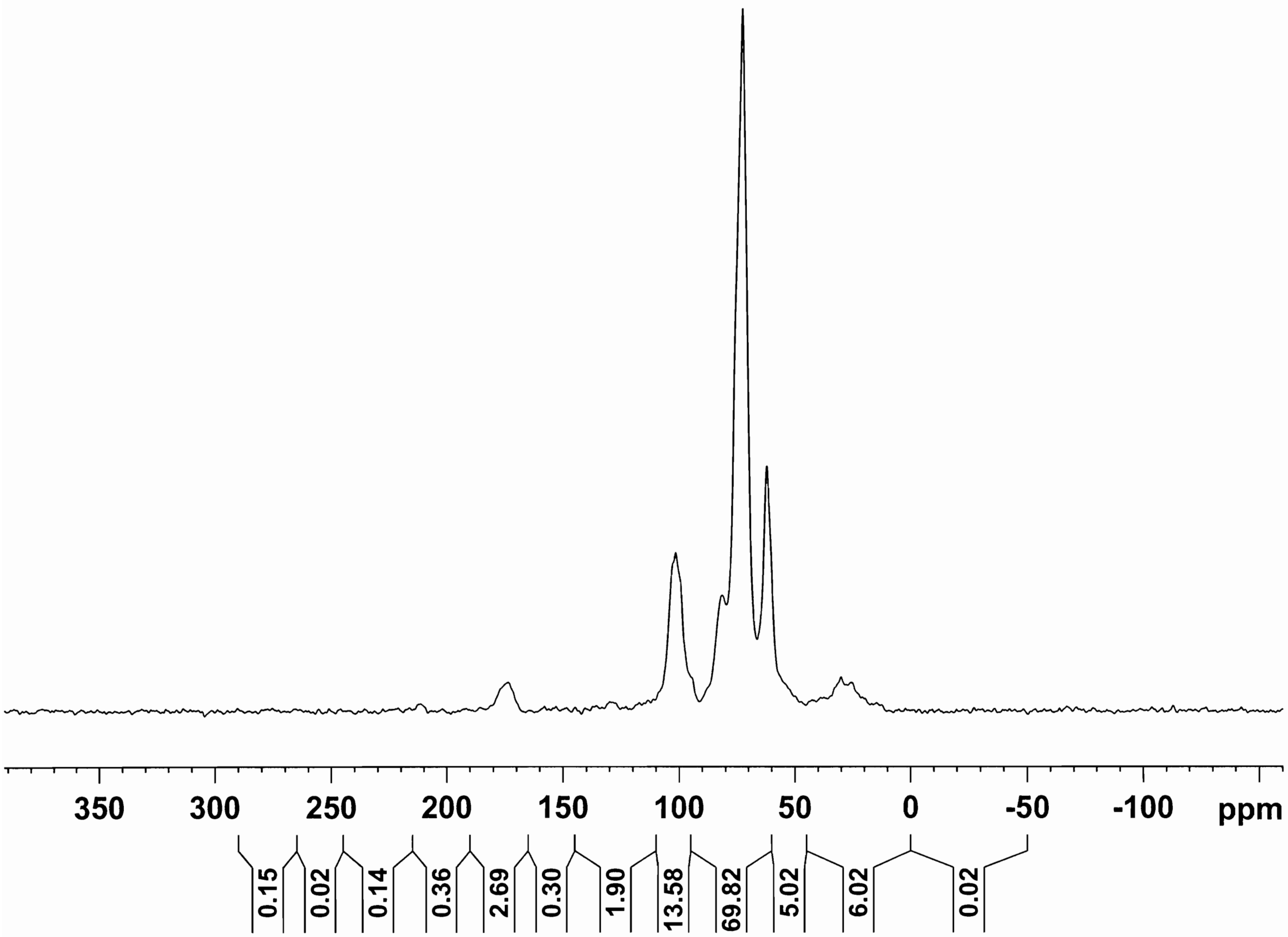
F2 - Acquisition Parameters
Date_ 20100318
Time 17.50
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1895
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 294.3 K
D1 3.00000000 sec
TD0 20

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.20 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.60 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228798 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 2 Wheat Grain (TRIGR)
03/19/2010   112.7 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBS 2004 T1R2 TRIGR
EXPNO   1
PROCNO   1

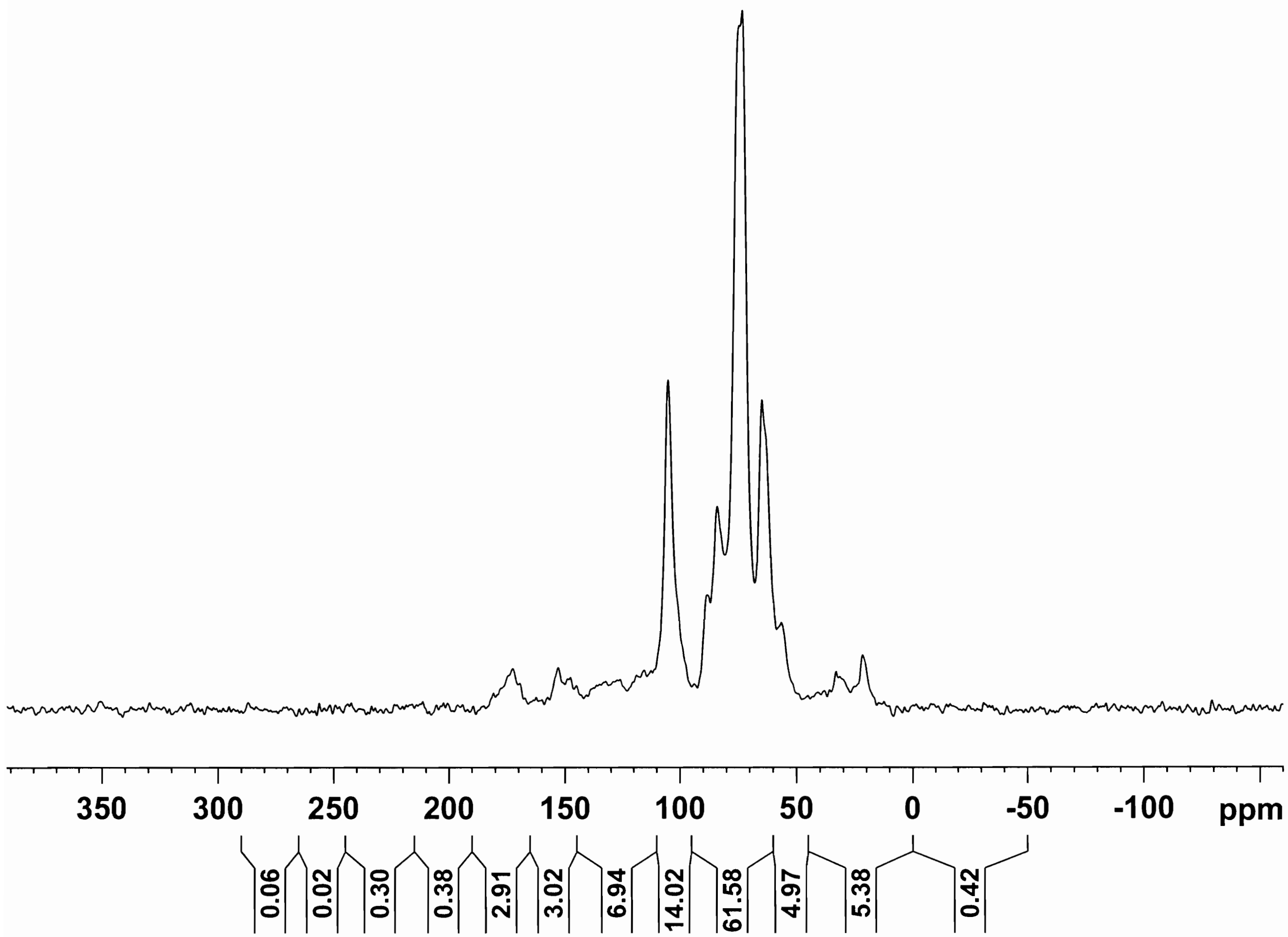
F2 - Acquisition Parameters
Date_   20100319
Time   8.52
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.WCH
TD   1024
SOLVENT
NS   1574
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   294.3 K
D1   3.00000000 sec
TD0   20

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.20 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.10 usec
P31   5.60 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228798 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 2 Wheat Stover (TRIST)
03/18/2010 65.4 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBS 2004 T1R2 TRIST
EXPNO 1
PROCNO 1

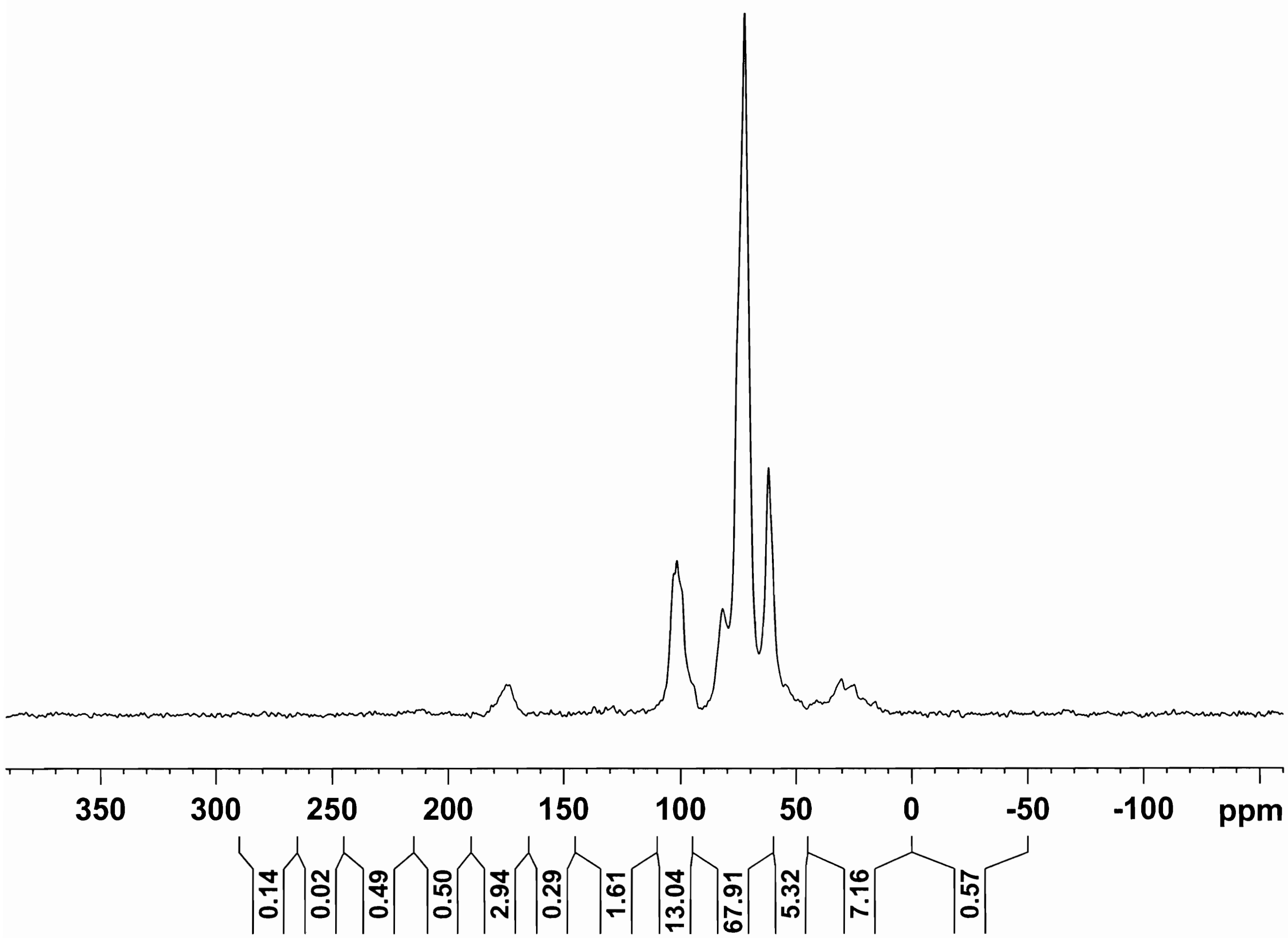
F2 - Acquisition Parameters
Date_ 20100318
Time 20.36
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 2000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 294.2 K
D1 3.00000000 sec
TD0 20

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.20 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.60 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228798 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 3 Wheat Grain (TRIGR)
04/21/2010   113.1 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBS 2004 T1R3 TRIGR
EXPNO   1
PROCNO   1

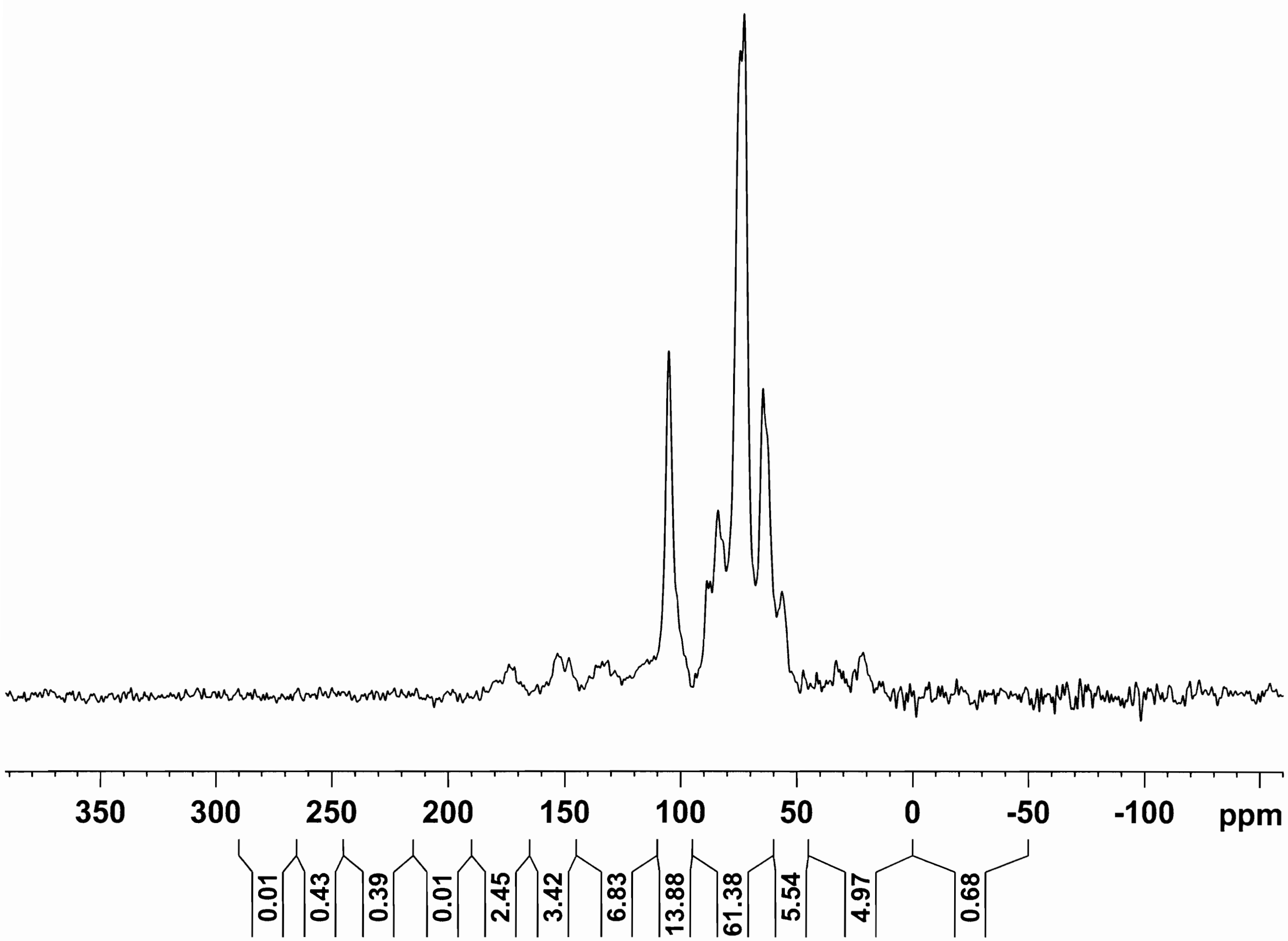
F2 - Acquisition Parameters
Date_   20100421
Time   10.16
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.WCH
TD   1024
SOLVENT
NS   1200
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   292.9 K
D1   3.00000000 sec
TD0   12

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.20 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.10 usec
P31   5.80 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228757 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Kellogg Biological Station Long Term Ecological Research Station
2004 Treatment 1 Replicate 3 Wheat Stover (TRIST)
04/21/2010   68.8 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBS 2004 T1R3 TRIST
EXPNO   1
PROCNO   1

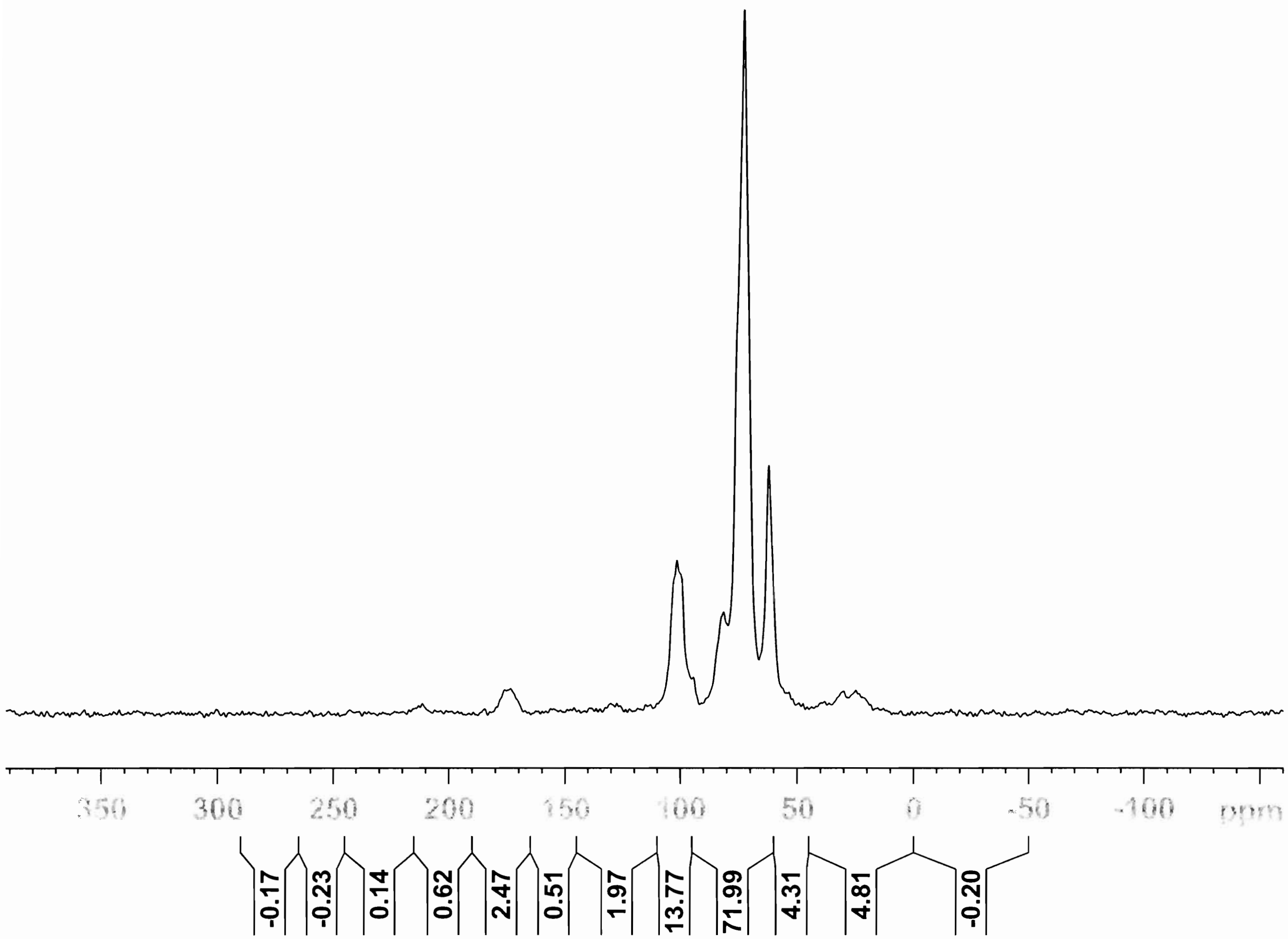
F2 - Acquisition Parameters
Date_   20100421
Time   14.59
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.WCH
TD   1024
SOLVENT
NS   1200
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   293.1 K
D1   3.00000000 sec
TD0   12

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.20 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.10 usec
P31   5.80 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228757 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 1 Corn Grain (ZEAGR)
04/21/2010   113.3 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBS 2005 T1R1 ZEAGR
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100421
Time	9.07
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1200
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.8 K
D1	3.00000000 sec
TD0	12

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.20 dB
SFO1	50.3287070 MHz

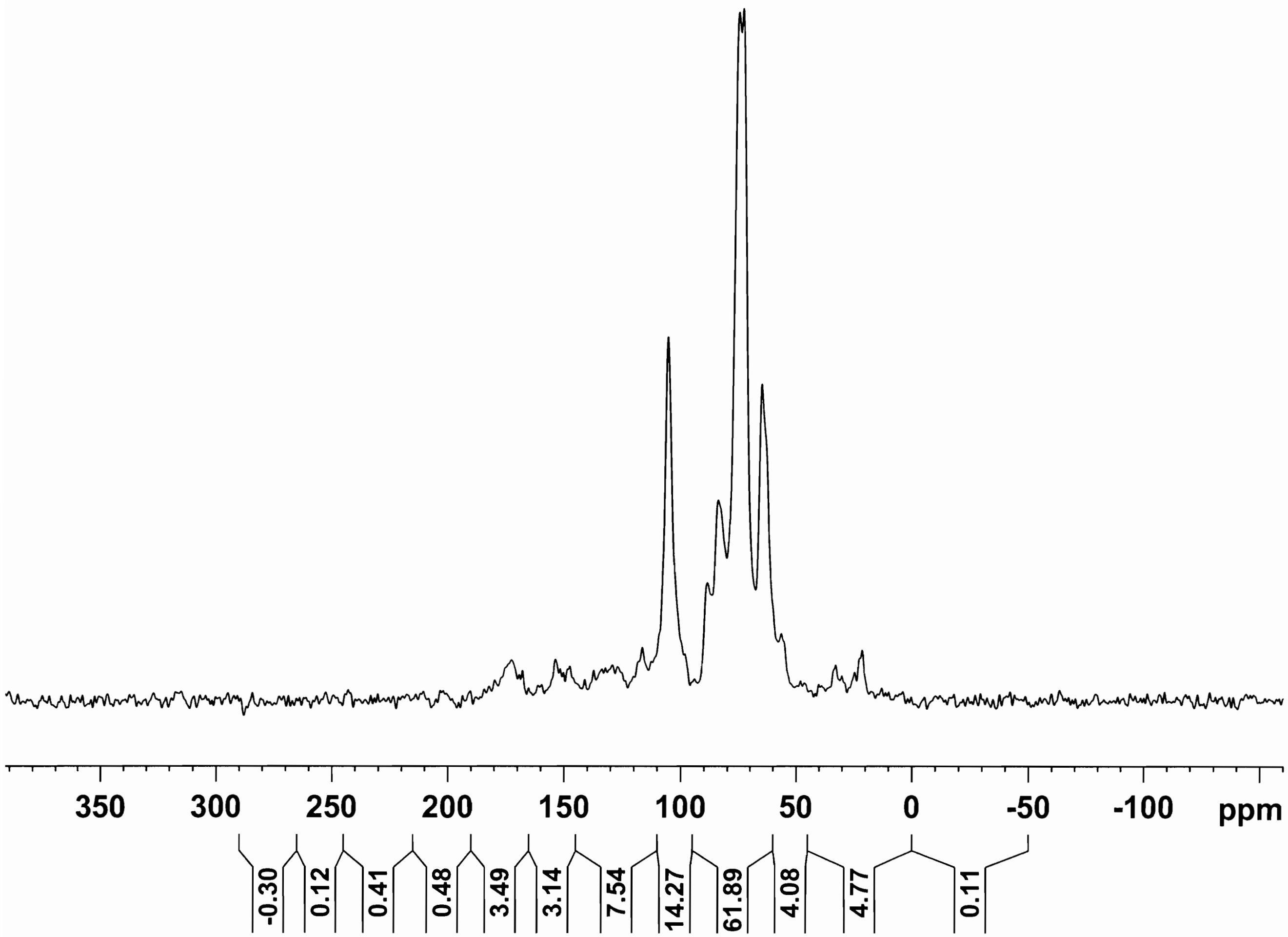
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.10 usec
P31	5.80 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228757 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 1 Corn Stover (ZEAST)
04/21/2010 62.7 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBS 2005 T1R1 ZEAST	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20100421	
Time	19.21	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1200	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	293.1	K
D1	3.00000000	sec
TD0	12	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.20	dB
SFO1	50.3287070	MHz

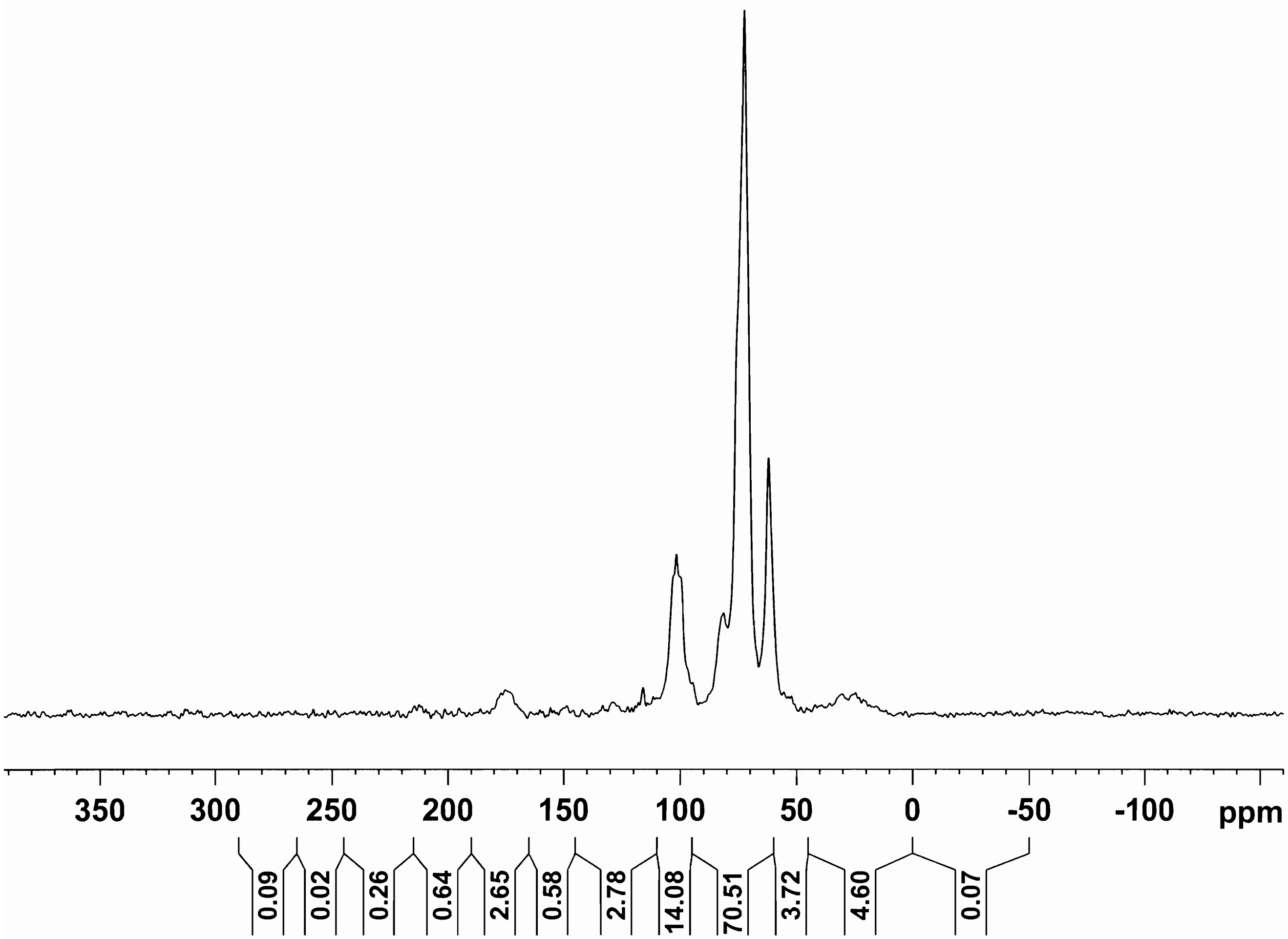
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.80	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228757	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 2 Corn Grain (ZEAGR)
04/21/2010   109.5 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBS 2005 T1R2 ZEAGR
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100421	
Time	12.42	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1200	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	293.1	K
D1	3.00000000	sec
TD0	12	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.20	dB
SFO1	50.3287070	MHz

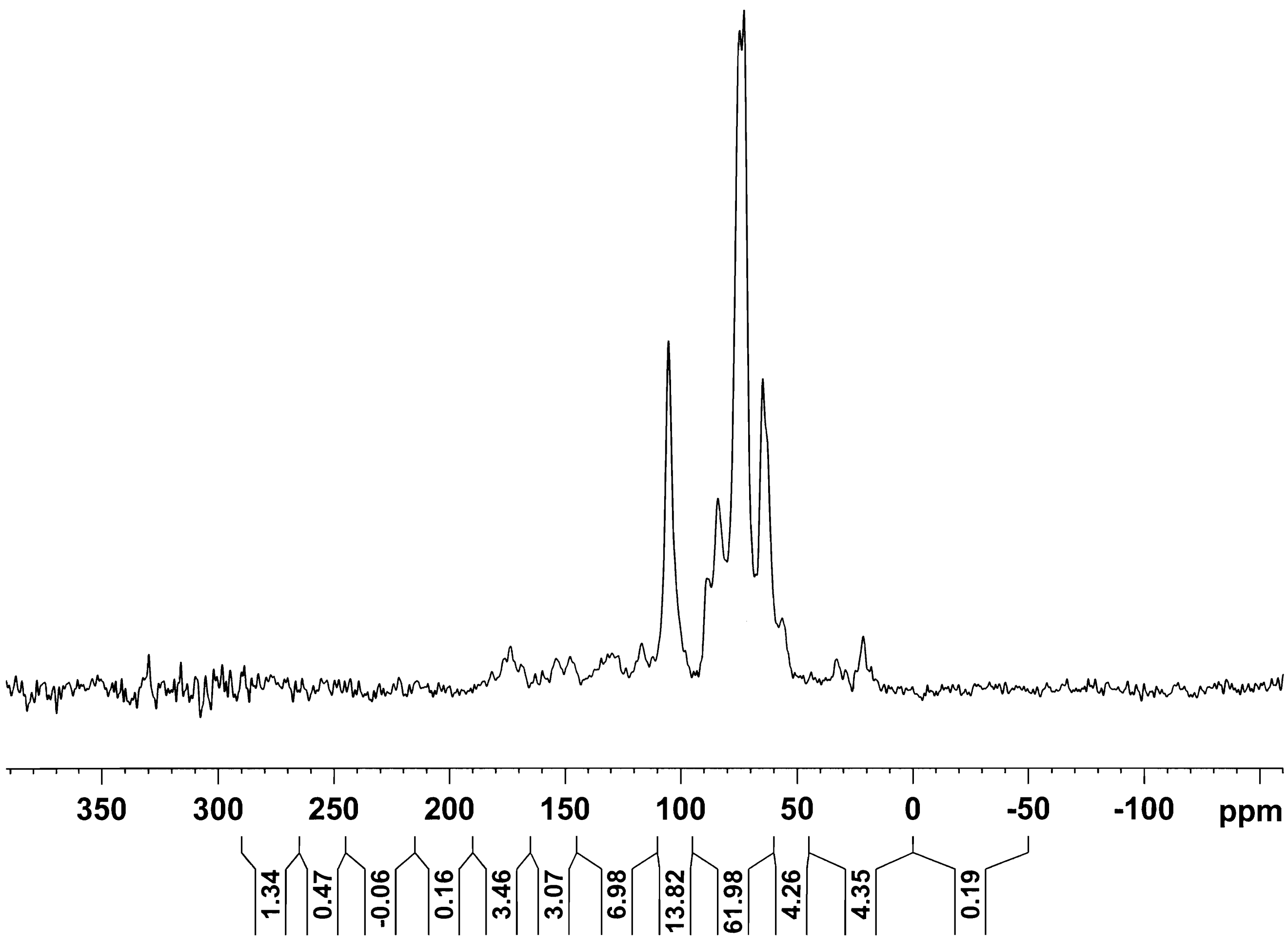
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.80	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228757	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 2 Corn Stover (ZEAST)
04/21/2010 61.0 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBS 2005 T1R2 ZEAST
EXPNO                   1
PROCNO                  1

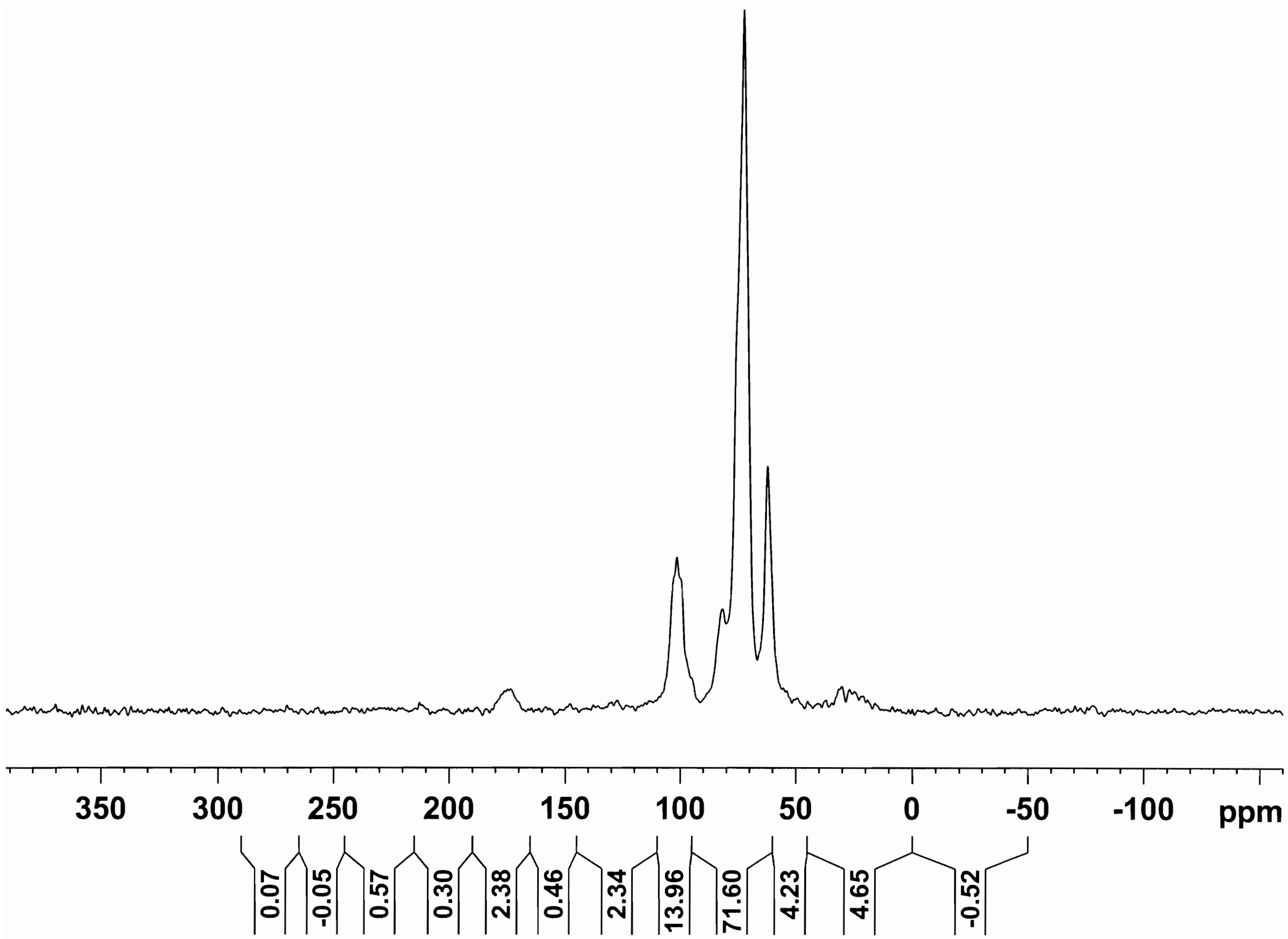
F2 - Acquisition Parameters
Date_            20100421
Time                18.09
INSTRUM             spect
PROBHD    4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                   1024
SOLVENT
NS                   1200
DS                      0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                   2048
DW                 18.000 usec
DE                  17.00 usec
TE                  293.1 K
D1             3.00000000 sec
TD0                    12

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  2.20 dB
SFO1           50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.10 usec
P31                  5.80 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3228757 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 3 Corn Grain (ZEAGR)
04/21/2010   114.1 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBS 2005 T1R3 ZEAGR	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20100421	
Time	13.51	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1200	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	293.1	K
D1	3.00000000	sec
TD0	12	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.20	dB
SFO1	50.3287070	MHz

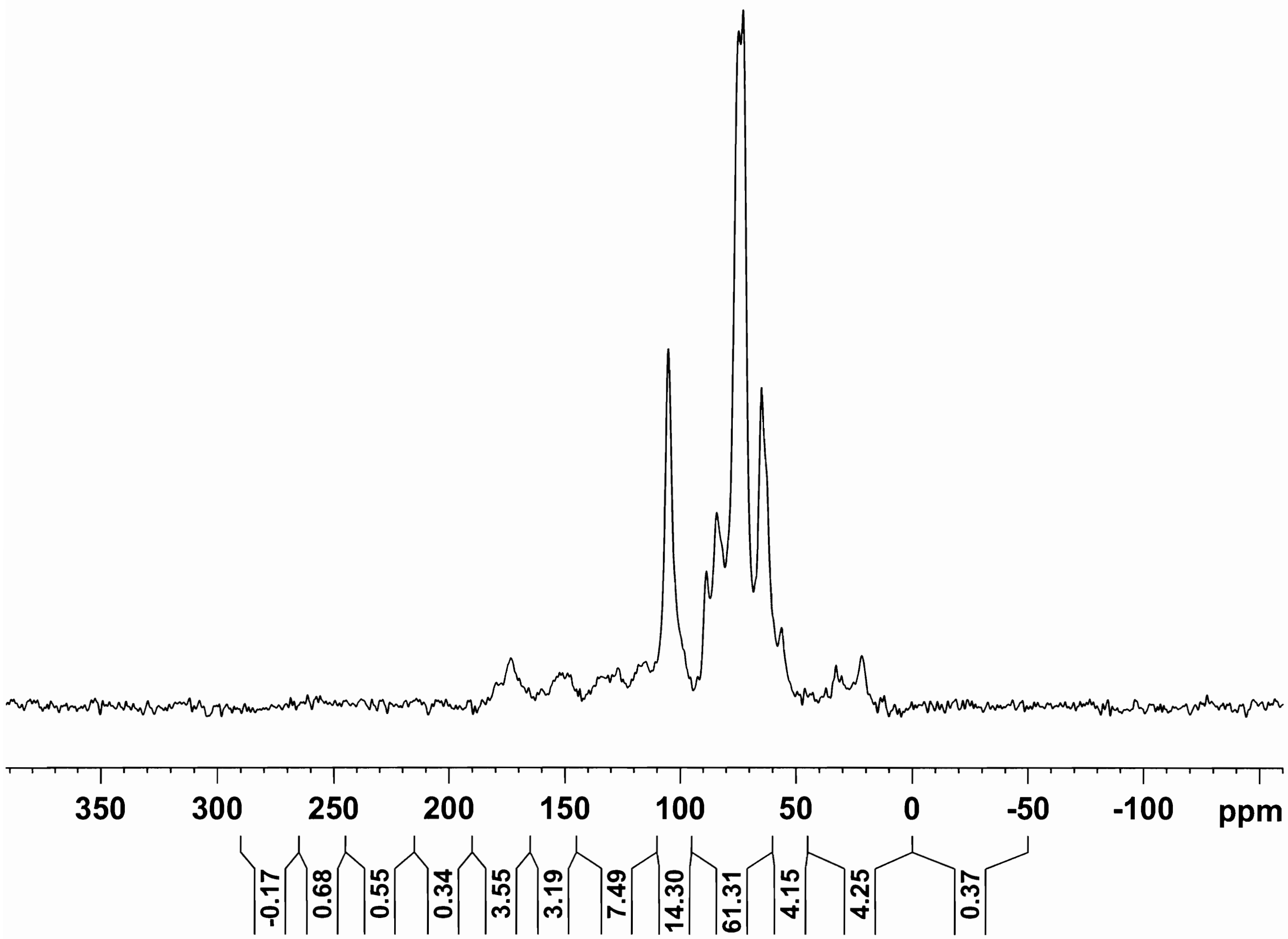
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.80	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228757	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Kellogg Biological Station Long Term Ecological Research Station
2005 Treatment 1 Replicate 3 Corn Stover (ZEAST)
04/21/2010   67.6 mg
4mm MAS probe. 7 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBS 2005 T1R3 ZEAST
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100421
Time               20.28
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                  1024
SOLVENT
NS                  1200
DS                     0
SWH            27777.777 Hz
FIDRES         27.126736 Hz
AQ             0.0185000 sec
RG                  2048
DW                18.000 usec
DE                 17.00 usec
TE                 292.9 K
D1            3.00000000 sec
TD0                   12

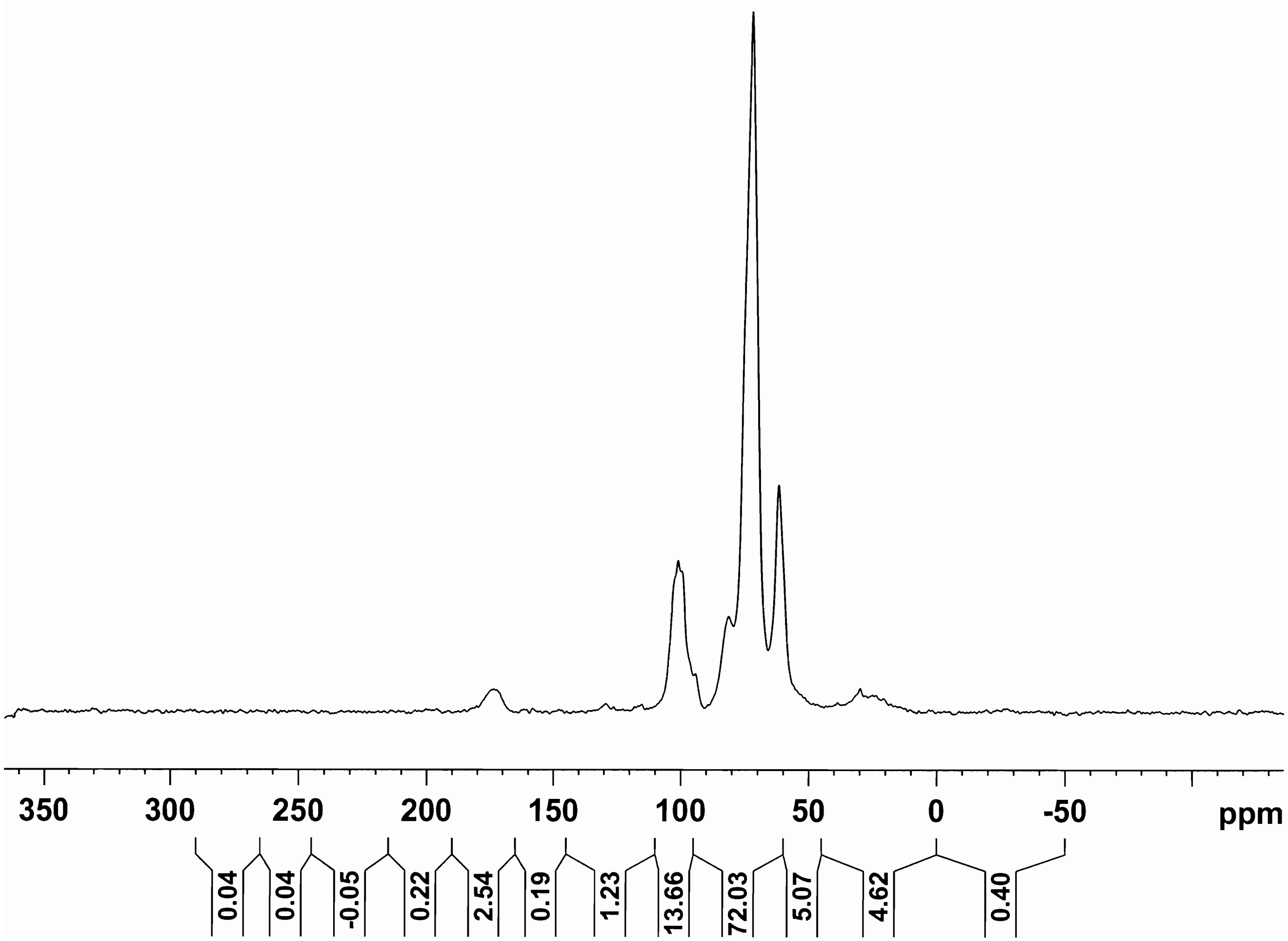
======== CHANNEL f1 ========
NUC1                 13C
P15              1000.00 usec
PL1                 2.20 dB
SFO1          50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2           tppm15
NUC2                  1H
P3                  3.10 usec
P31                 5.80 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3228757 MHz
WDW                   EM
SSB                    0
LB                 30.00 Hz
GB                     0
PC                  1.00
```

Figure D2. Nitrogen Rate Experiment

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Grain, Treatment 0 kg N/ha, Replicate 1, Cover Crop
03/13/2008 109.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain101_1A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20071026
Time	11.29
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2896.3
DW	19.800 usec
DE	6.00 usec
TE	698.0 K
D1	2.00000000 sec

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz

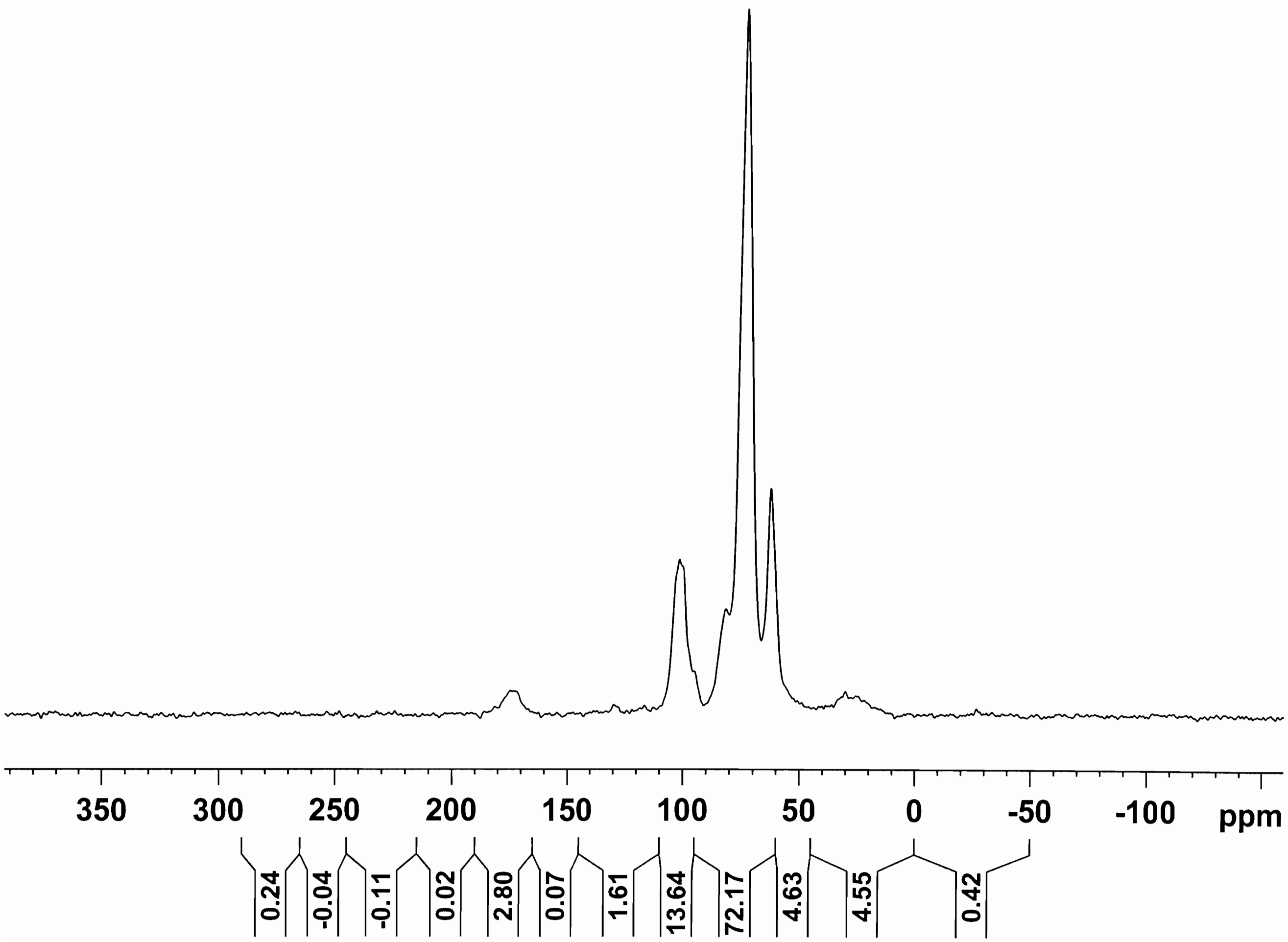
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.10 usec
P31	5.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229197 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1A Grain, Treatment 0 kg N/ha, Replicate 2, Cover Crop
11/27/2009   108.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_Grain203_1A
EXPNO 1
PROCNO 1

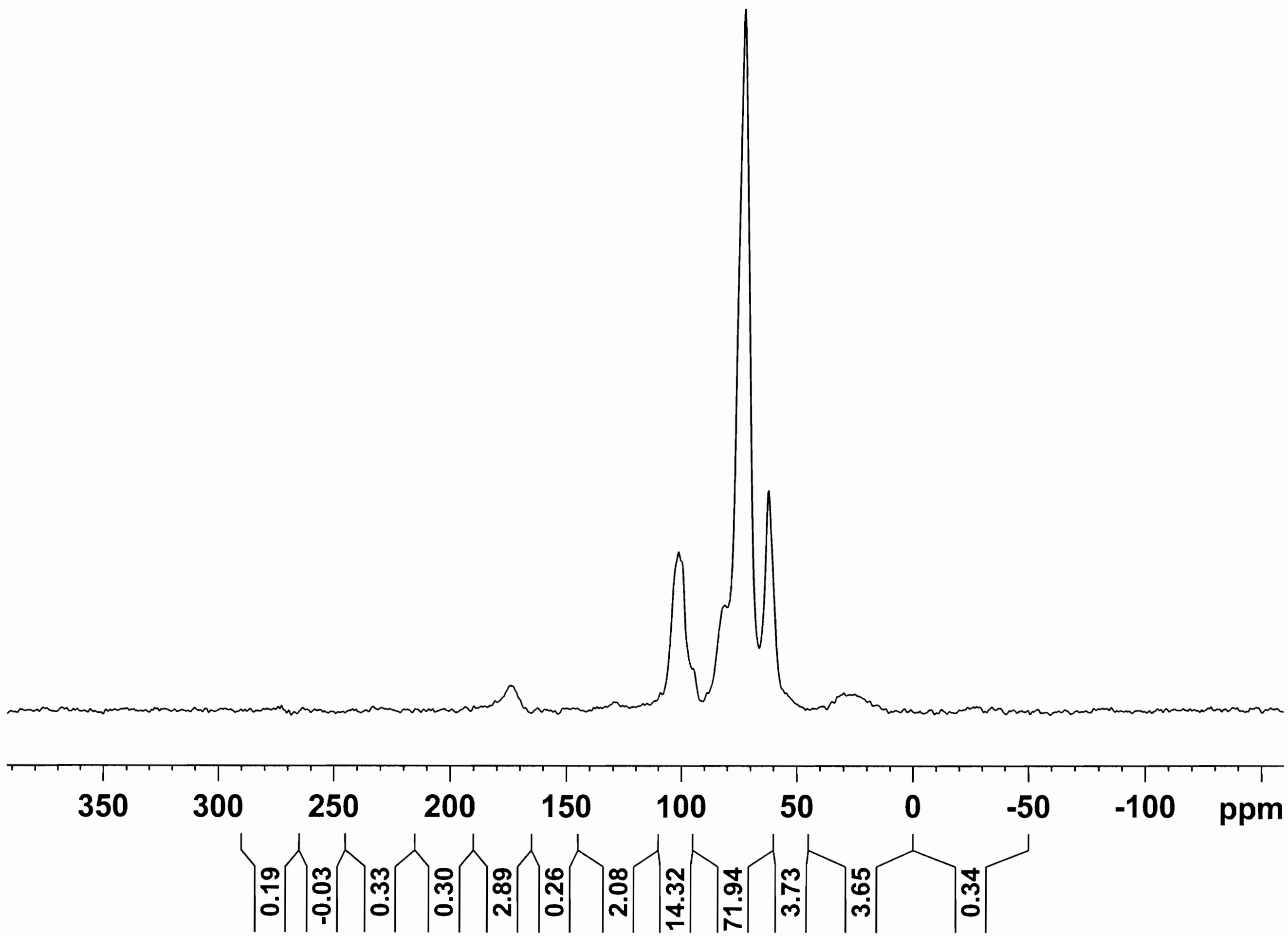
F2 - Acquisition Parameters
Date_ 20091127
Time 14.09
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1A Grain, Treatment 0 kg N/ha, Replicate 3, Cover Crop
11/27/2009   109.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_Grain307_1A
EXPNO 1
PROCNO 1

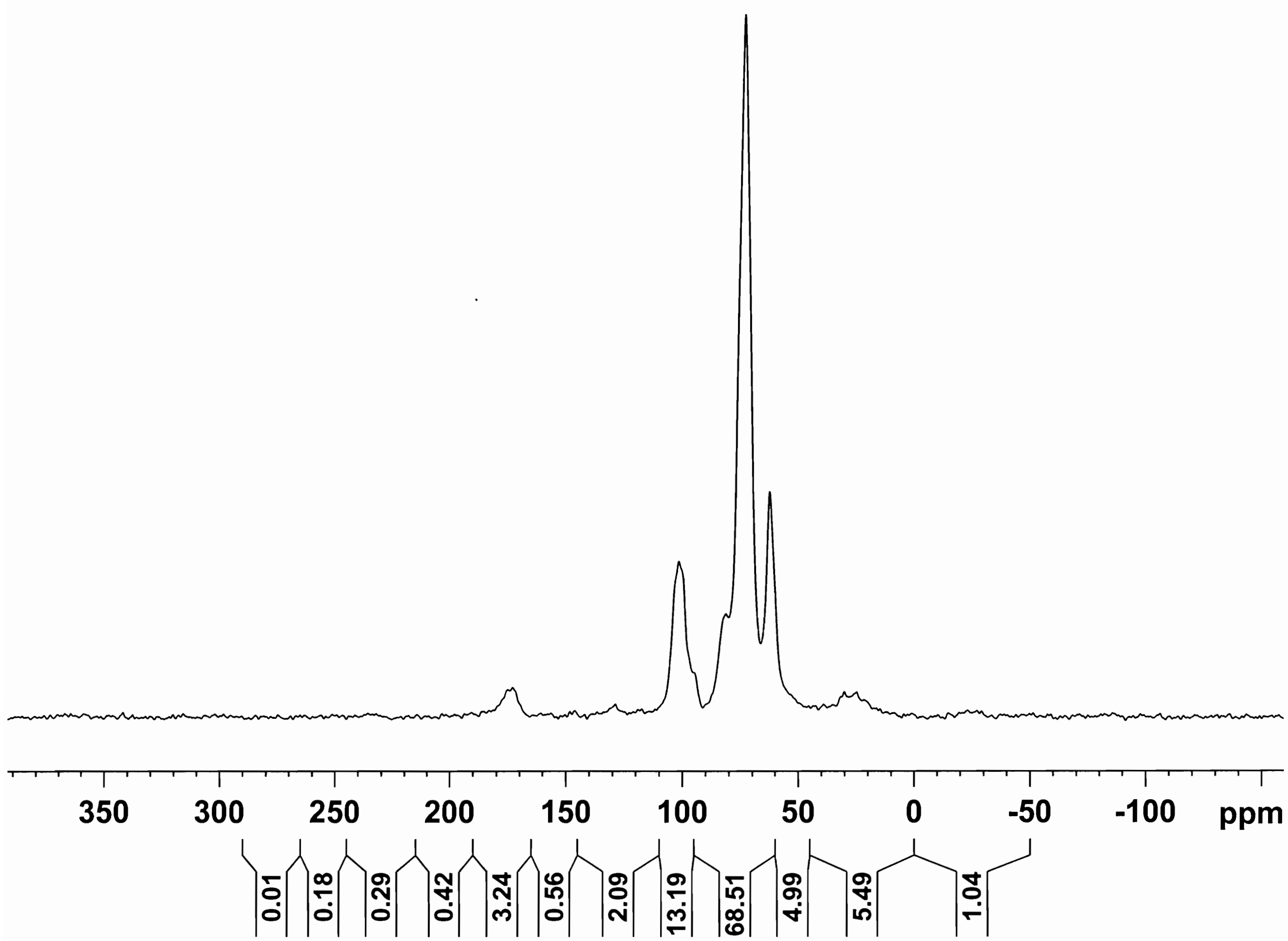
F2 - Acquisition Parameters
Date_ 20091127
Time 17.39
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1A Grain, Treatment 0 kg N/ha, Replicate 4, Cover Crop
11/27/2009   110.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain402_1A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091127
Time	18.36
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.1 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

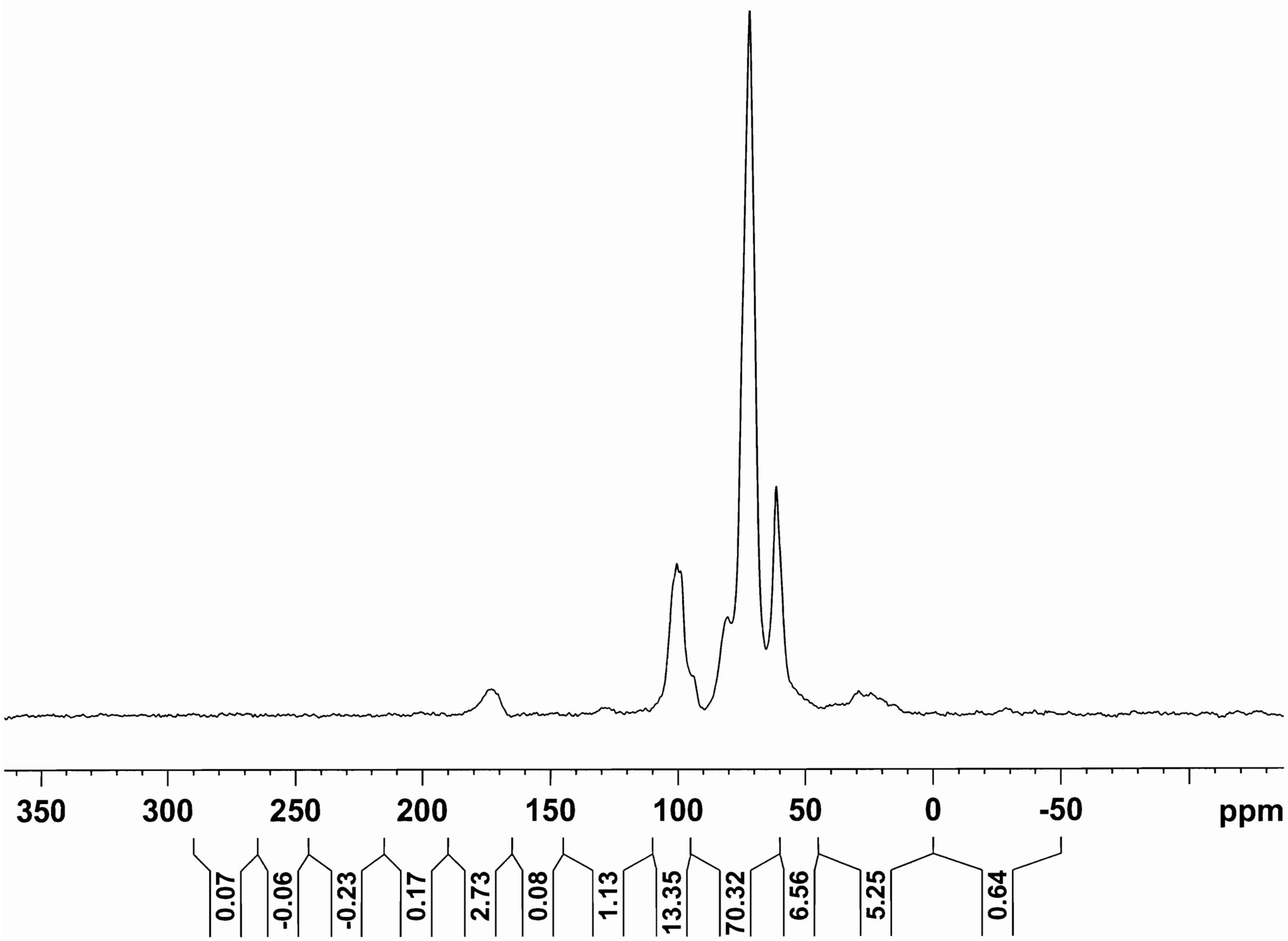
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Grain, Treatment 34 kg N/ha, Replicate 1, Cover Crop
03/03/2008   103.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_Grain107_2A
EXPNO                    1
PROCNO                   1

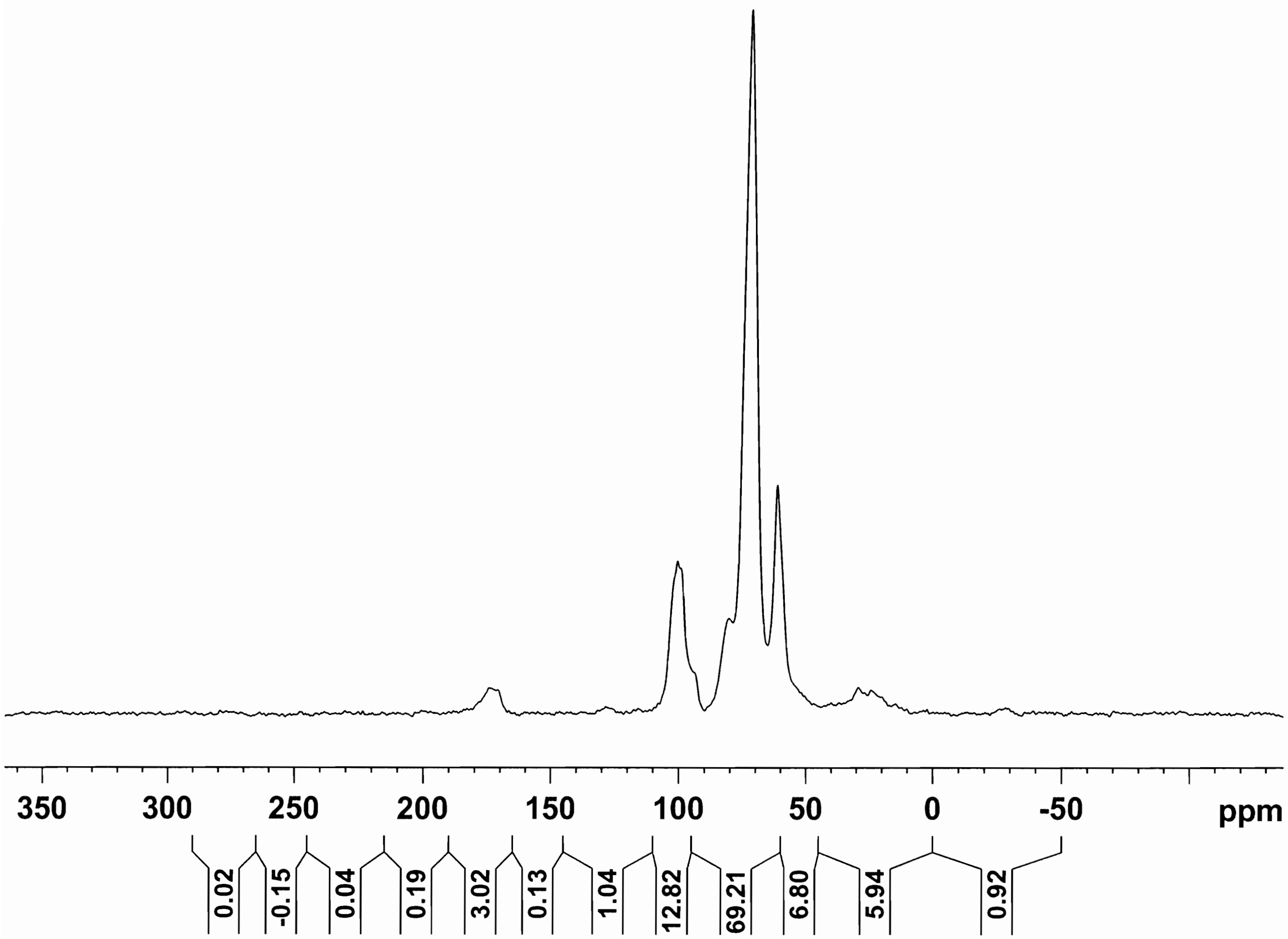
F2 - Acquisition Parameters
Date_             20080304
Time                 10.55
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                    8192
DW                  19.800 usec
DE                    6.00 usec
TE                   697.8 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.05 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229662 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Grain, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/05/2008   103.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_Grain106_3A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_	20080305
Time	2.19
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	724.1
DW	19.800 usec
DE	6.00 usec
TE	697.8 K
D1	2.00000000 sec

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz

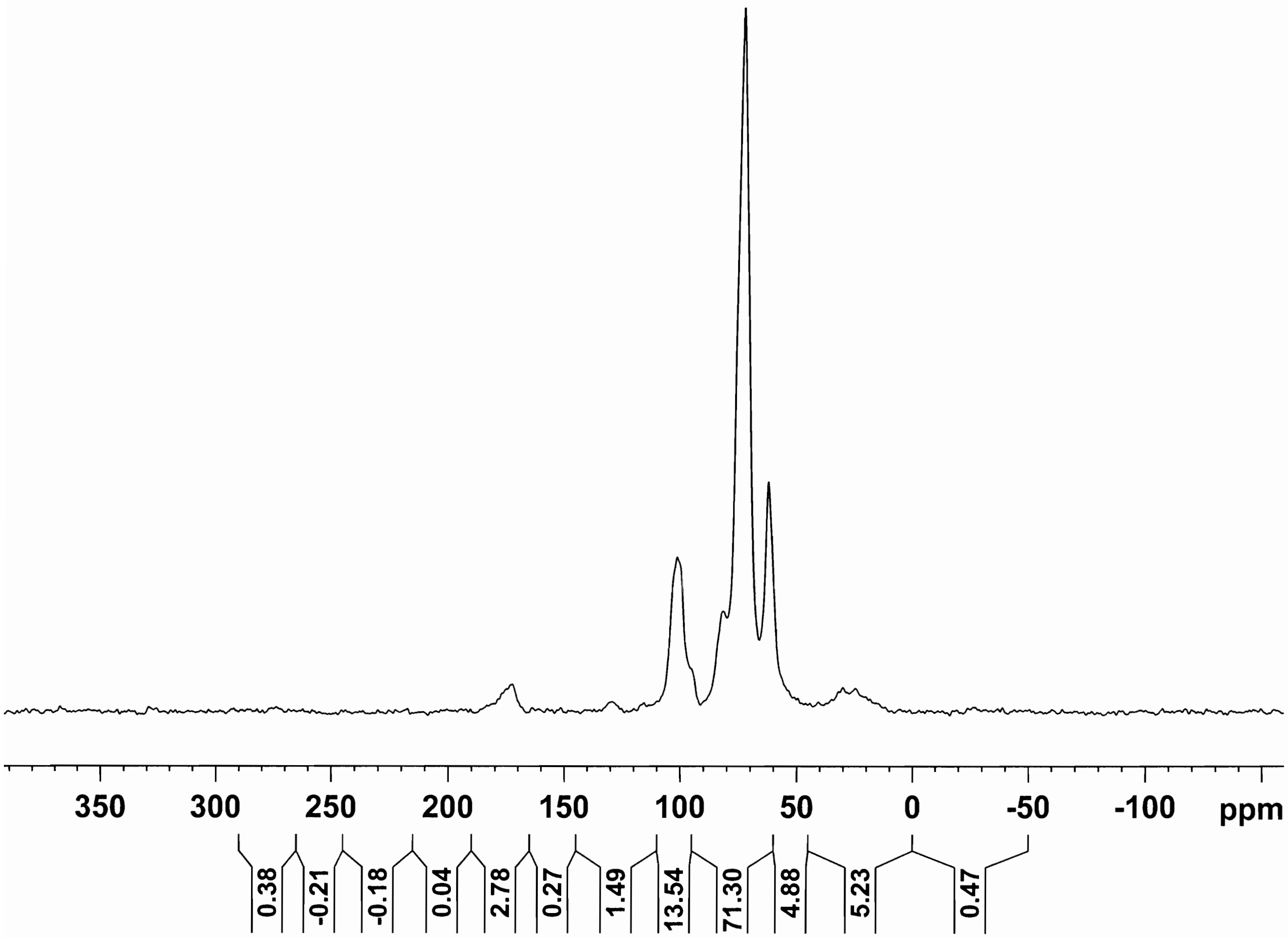
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229662 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3A Grain, Treatment 67 kg N/ha, Replicate 2, Cover Crop
11/27/2009   113.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_Grain202_3A
EXPNO 1
PROCNO 1

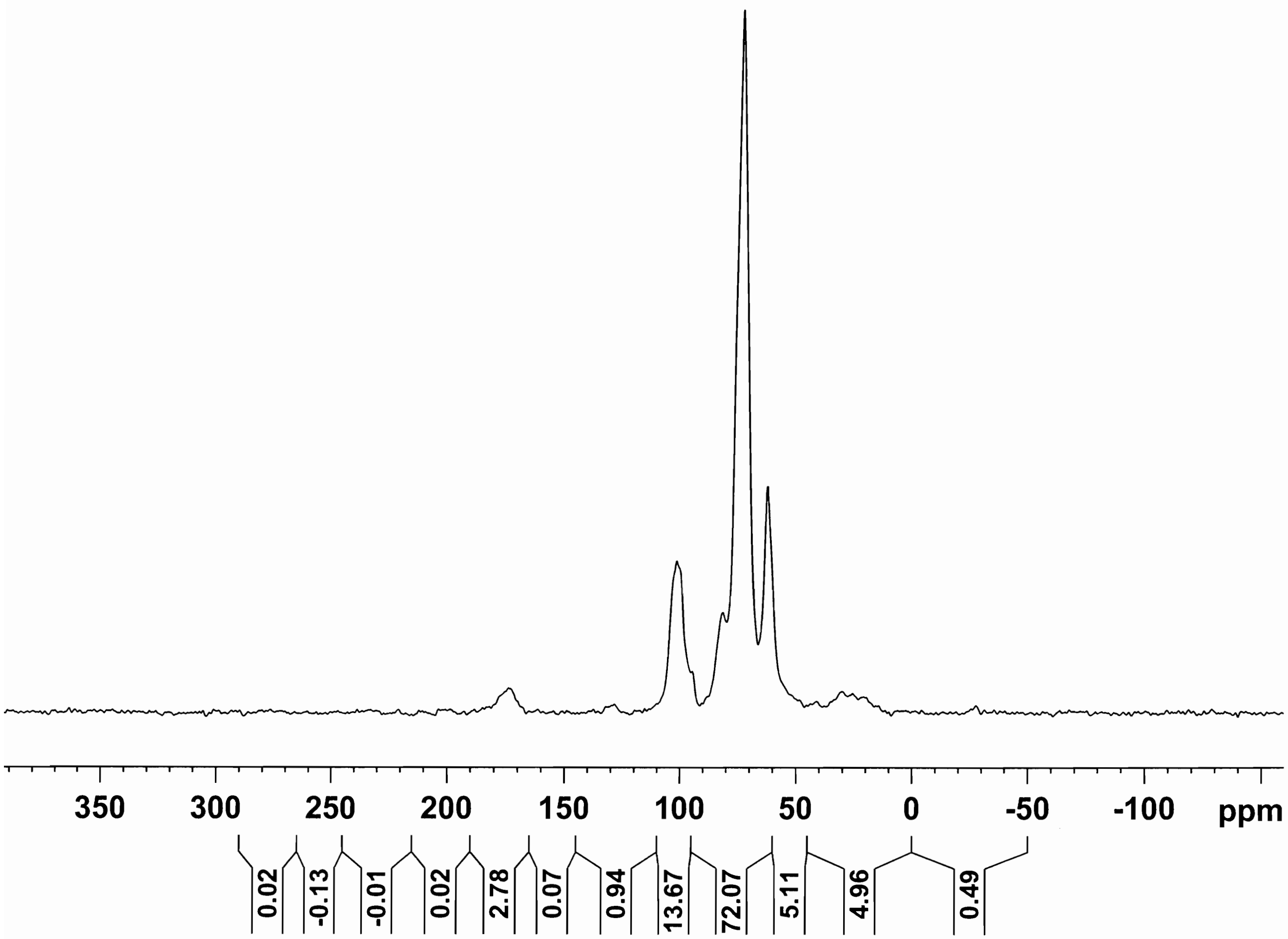
F2 - Acquisition Parameters
Date_ 20091127
Time 12.13
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3A Grain, Treatment 67 kg N/ha, Replicate 3, Cover Crop
11/27/2009   113.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_Grain305_3A
EXPNO                        1
PROCNO                       1

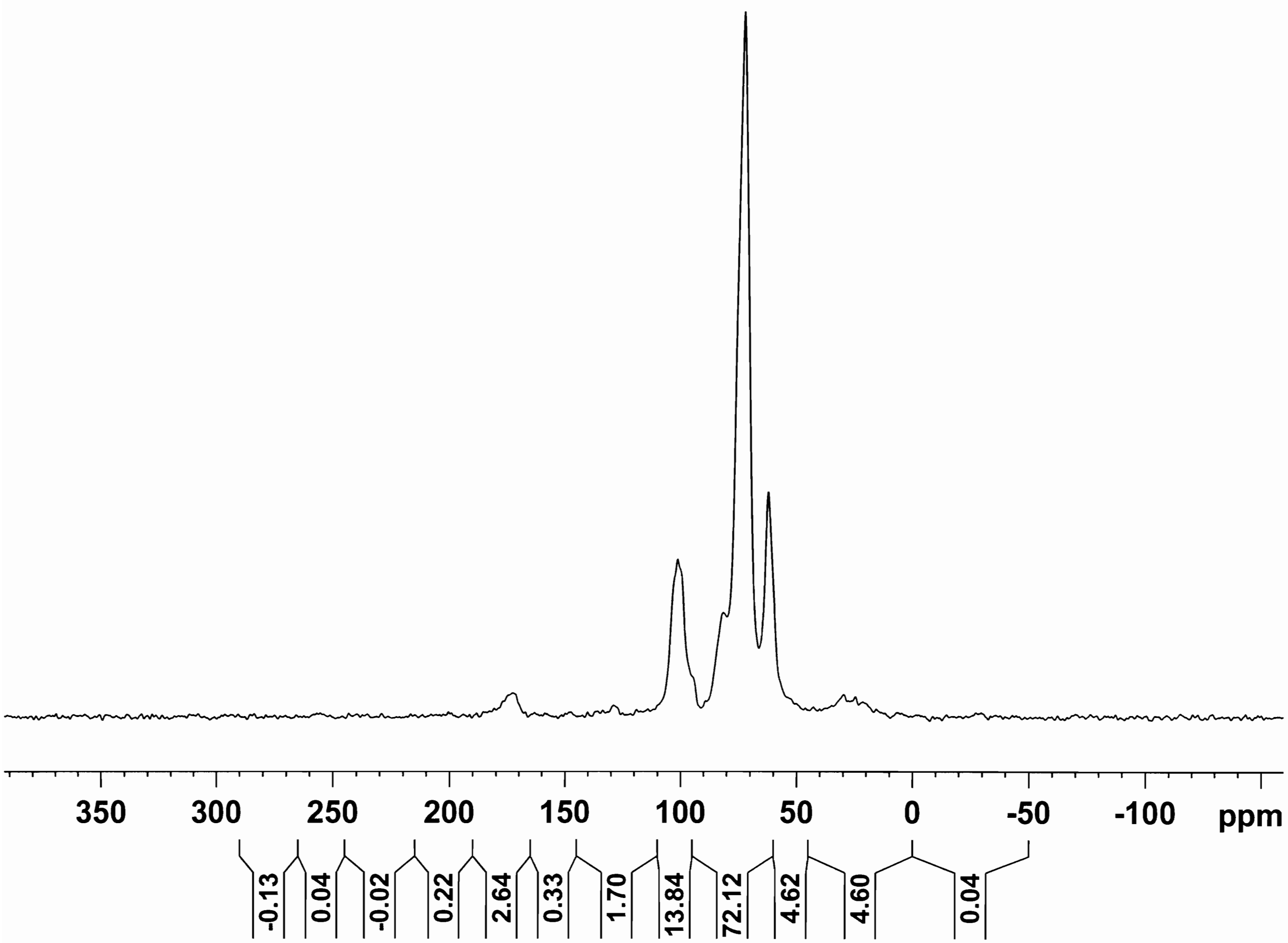
F2 - Acquisition Parameters
Date_             20091127
Time                 13.12
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   292.1 K
D1              3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3A Grain, Treatment 67 kg N/ha, Replicate 4, Cover Crop
11/15/2009 109.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_Grain404_3A
EXPNO 1
PROCNO 1

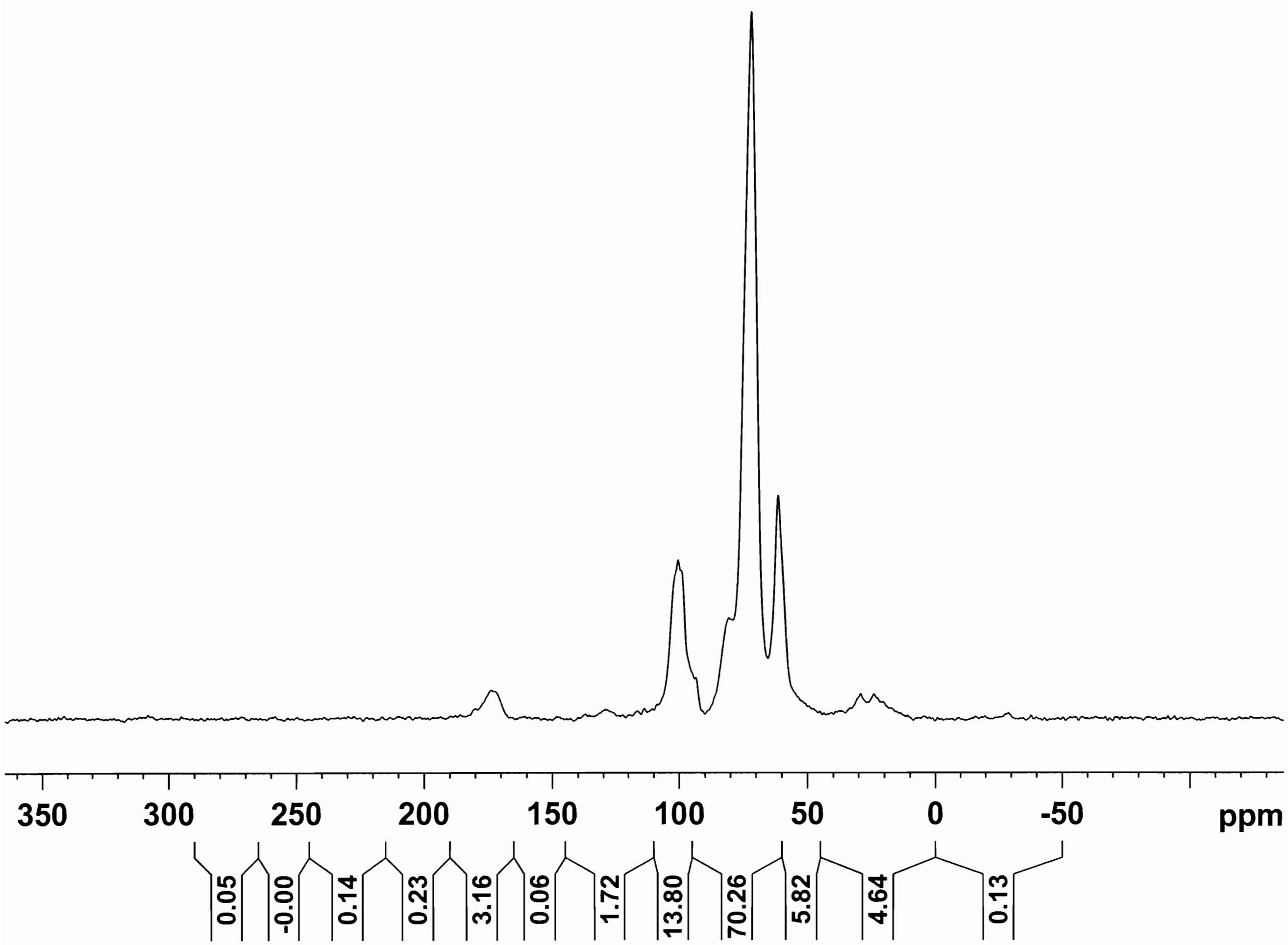
F2 - Acquisition Parameters
Date_ 20091115
Time_ 17.40
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.4 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

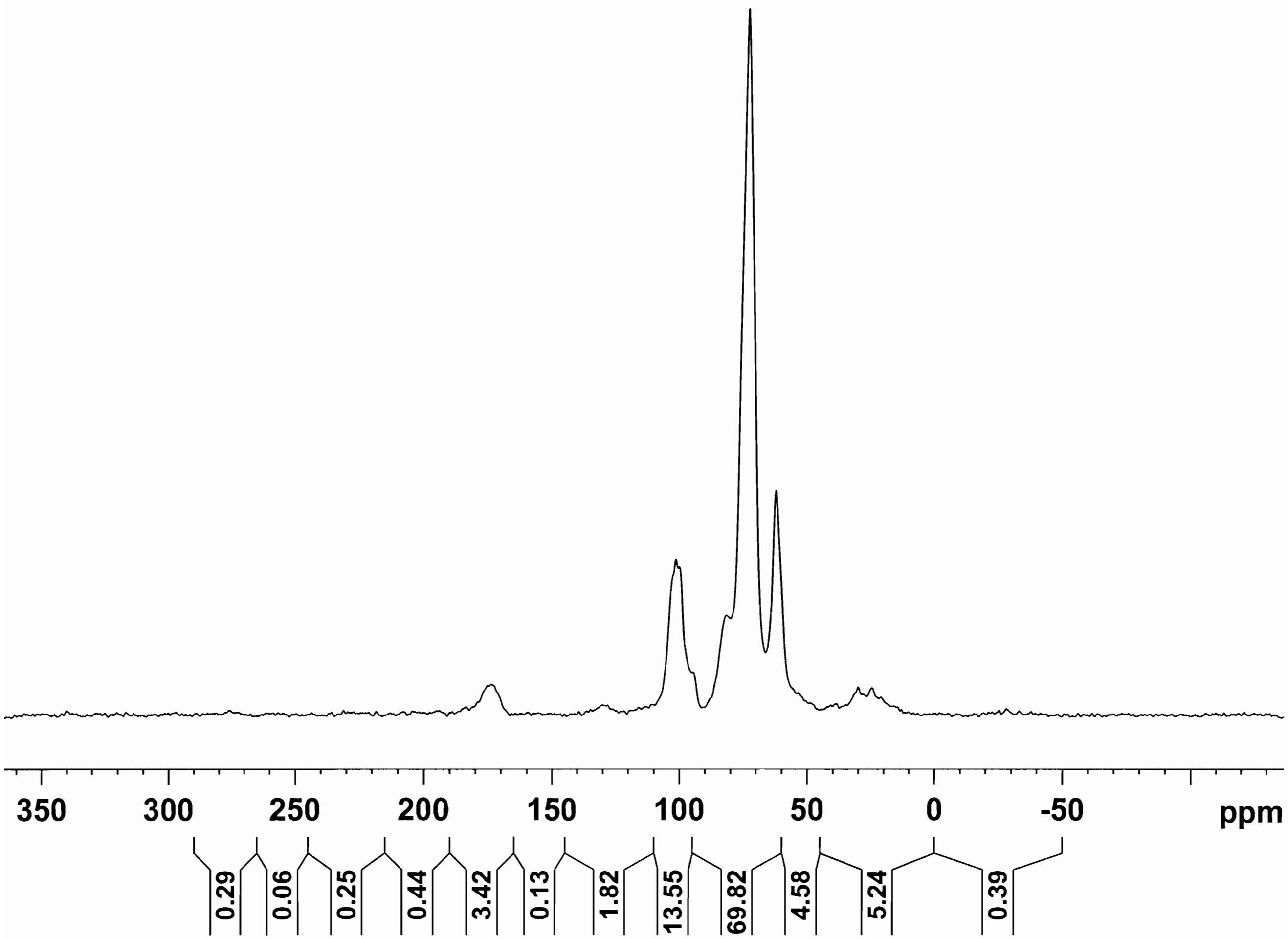
F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Grain, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/05/2008   111.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters		
NAME	KBSNRate_Grain102_4A	
EXPNO	1	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20080305	
Time	17.06	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	1625.5	
DW	19.800	usec
DE	6.00	usec
TE	697.9	K
D1	2.00000000	sec
======== CHANNEL f1 ========		
NUC1	13C	
P15	1000.00	usec
PL1	1.40	dB
SFO1	50.3287071	MHz
======== CHANNEL f2 ========		
CPDPRG2	tppm15	
NUC2	1H	
P3	3.05	usec
P31	5.10	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz
F2 - Processing parameters		
SI	16384	
SF	50.3229662	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Grain, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/06/2008   103.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME   KBSNRate_Grain104_5A
EXPNO   1
PROCNO   1

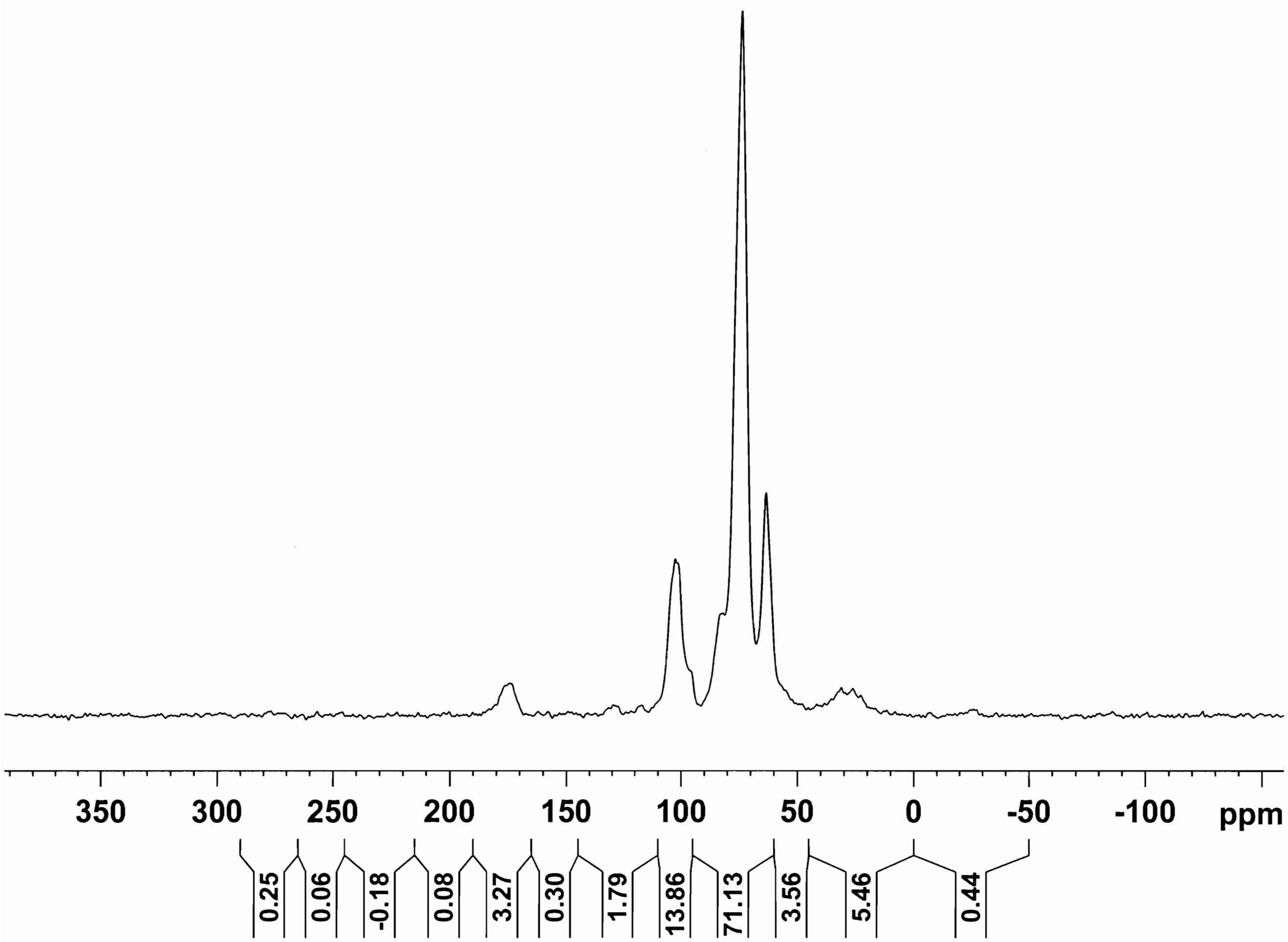
F2 - Acquisition Parameters
Date_   20080306
Time   13.29
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   1625.5
DW   19.800 usec
DE   6.00 usec
TE   694.9 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229662 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5A Grain, Treatment 134 kg N/ha, Replicate 2, Cover Crop
01/04/2010   110.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_Grain205_5A
EXPNO                    1
PROCNO                   1

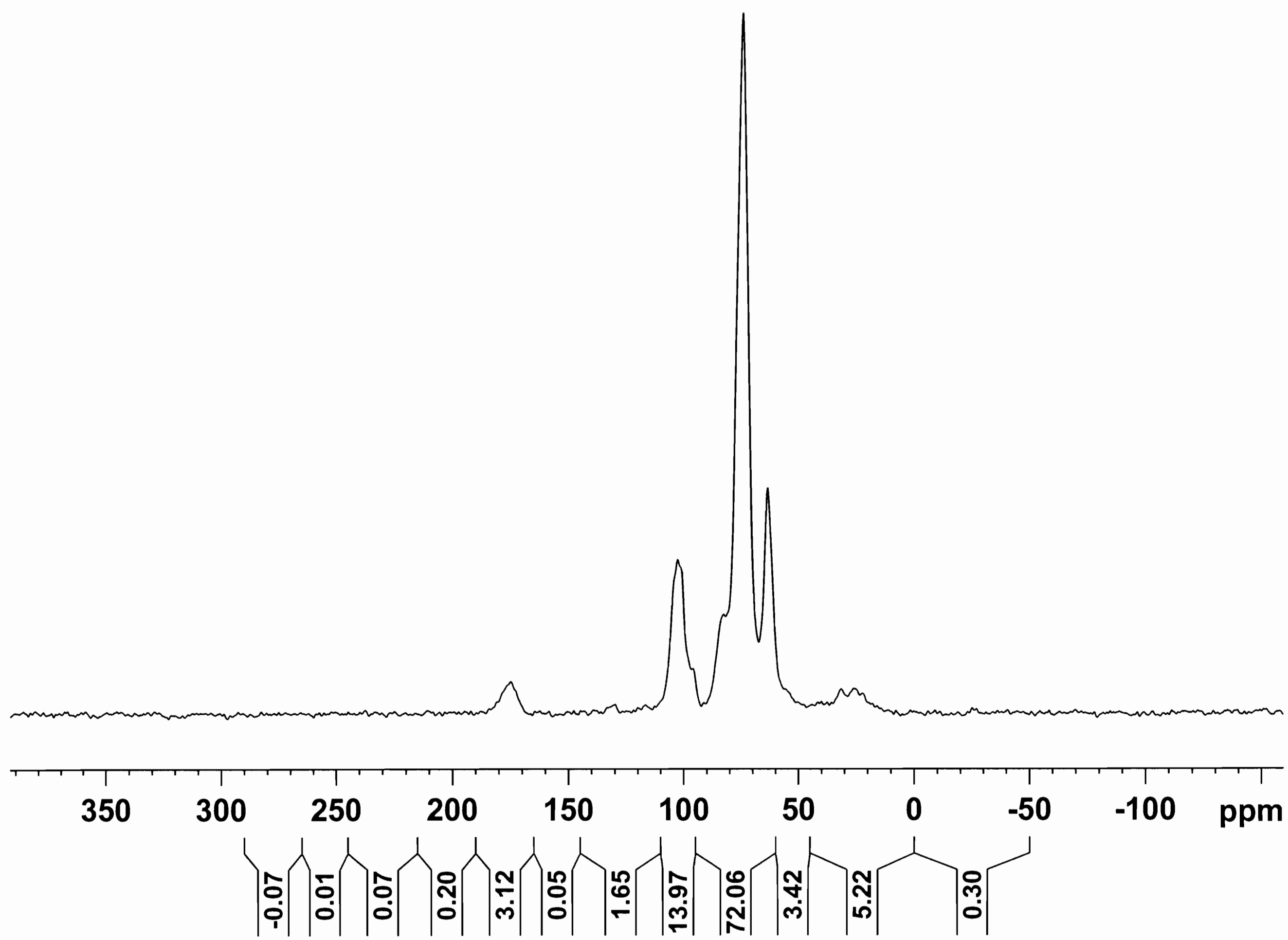
F2 - Acquisition Parameters
Date_             20100104
Time                 11.26
INSTRUM              spect
PROBHD     4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   291.5 K
D1              3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5A Grain, Treatment 134 kg N/ha, Replicate 3, Cover Crop
01/04/2010   108.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_Grain302_5A
EXPNO 1
PROCNO 1

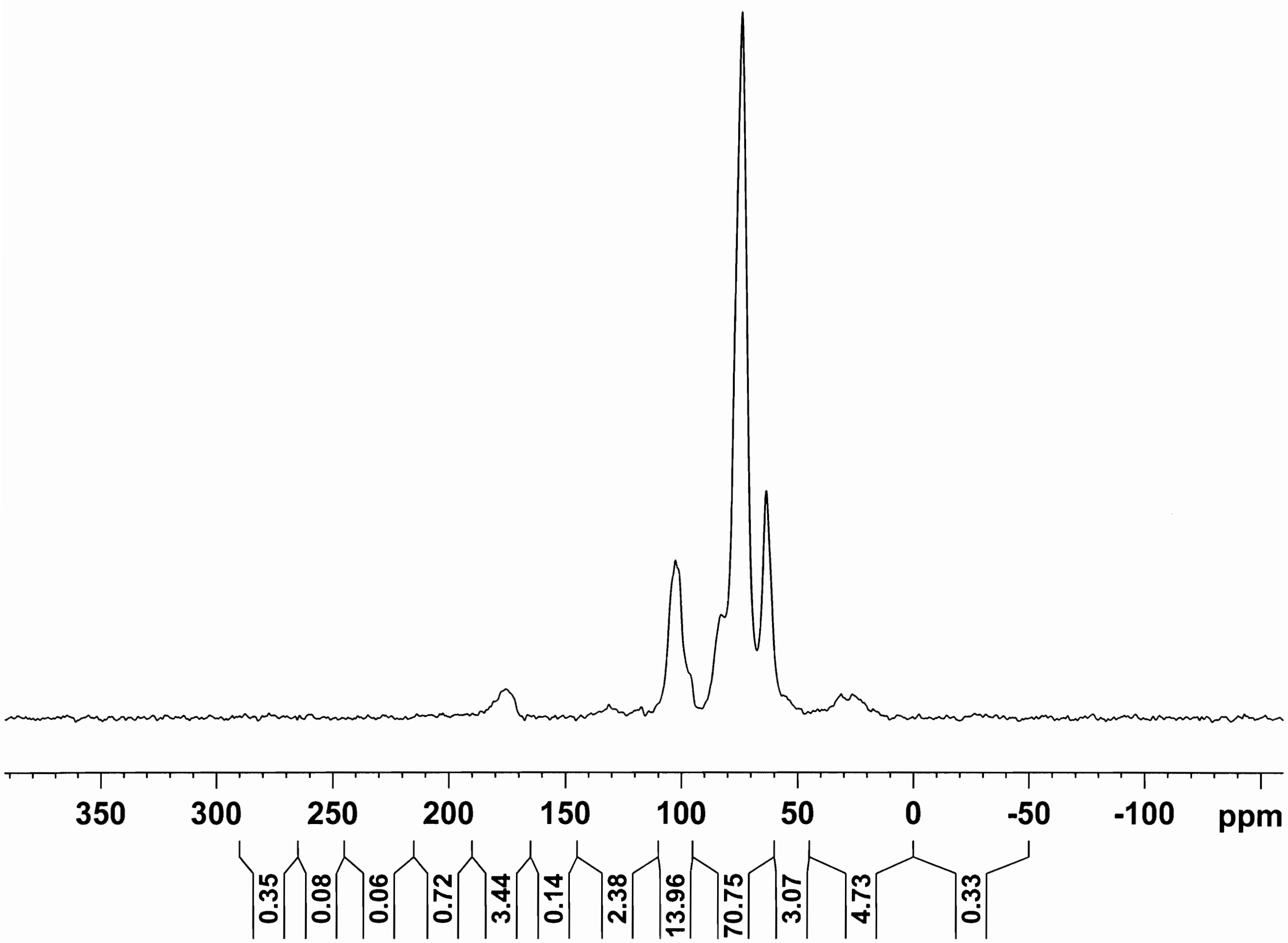
F2 - Acquisition Parameters
Date_ 20100104
Time 12.23
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 291.7 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5A Grain, Treatment 134 kg N/ha, Replicate 4, Cover Crop
01/04/2010   114.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME   KBSNRate_Grain407_5A
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters

Date_	20100104
Time	13.22
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	291.6 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

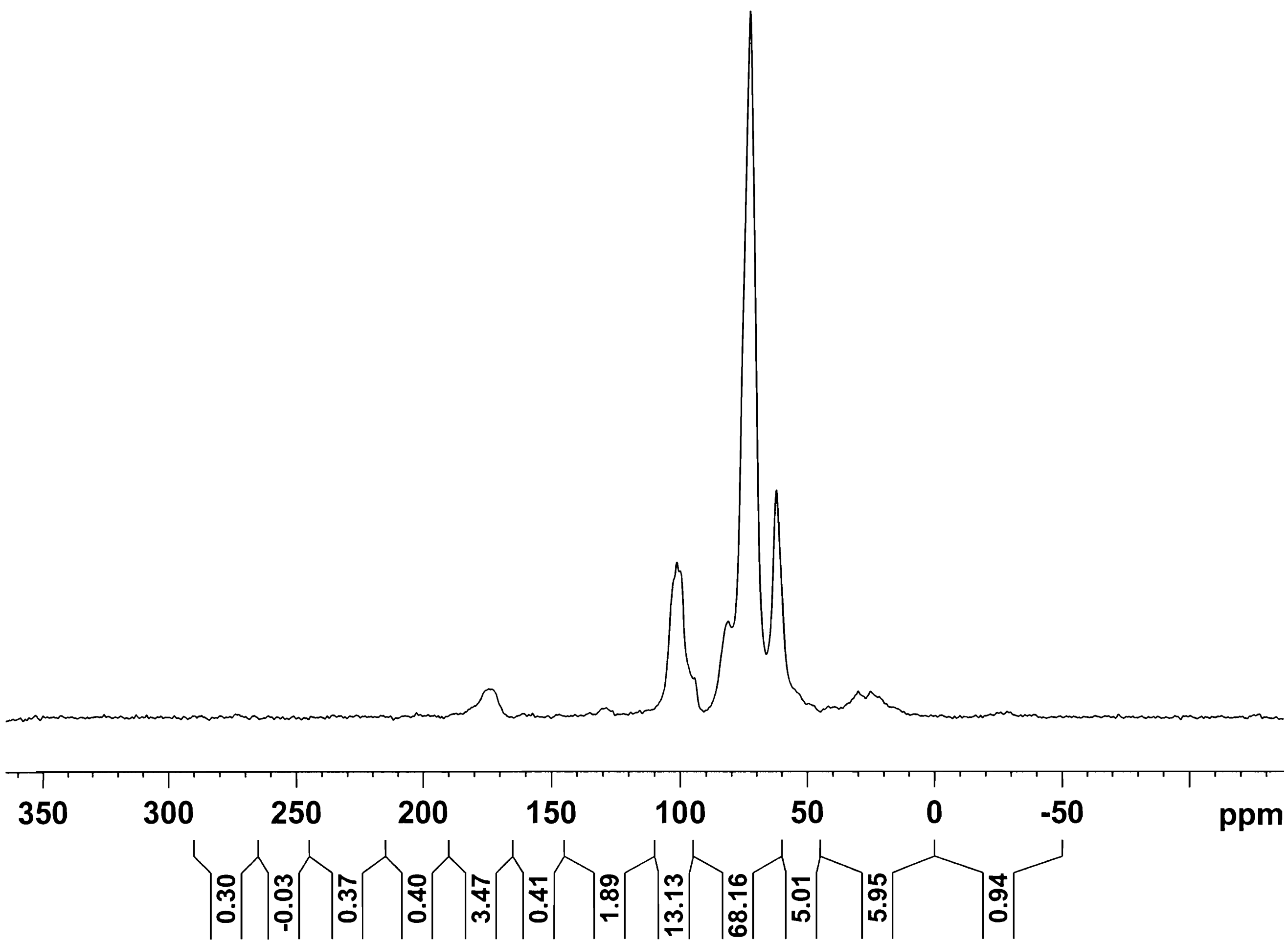
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Grain, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/07/2008   102.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME   KBSNRate_Grain103_6A
EXPNO   1
PROCNO   1

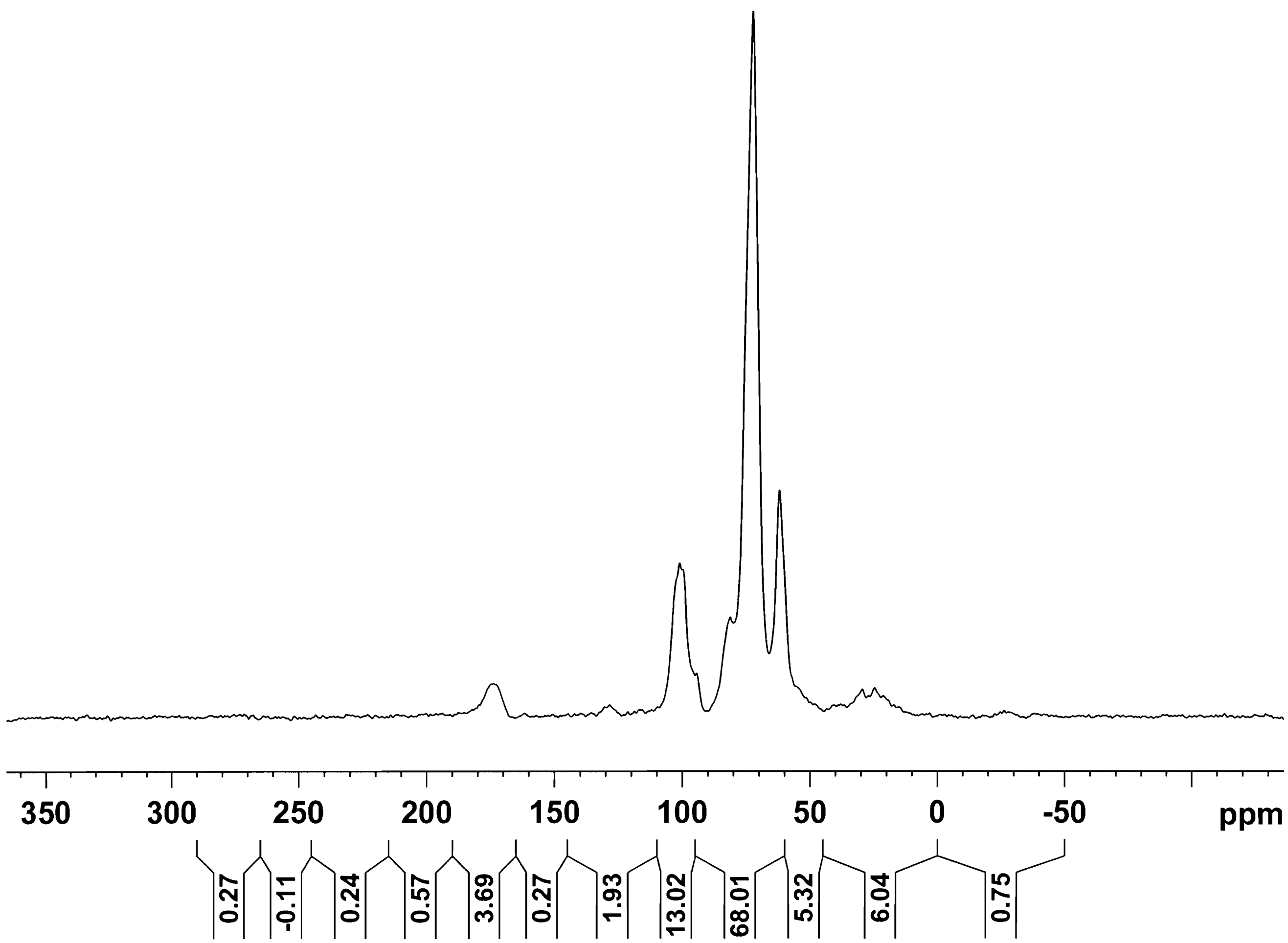
F2 - Acquisition Parameters
Date_   20080307
Time   4.46
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   1625.5
DW   19.800 usec
DE   6.00 usec
TE   694.2 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229662 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Grain, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/14/2008   101.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain105_7A	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20080214	
Time	18.31	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	1625.5	
DW	19.800	usec
DE	6.00	usec
TE	696.2	K
D1	2.00000000	sec

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	1.40	dB
SFO1	50.3287071	MHz

======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3229348	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7A Grain, Treatment 202 kg N/ha, Replicate 2, Cover Crop
11/27/2009   107.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.

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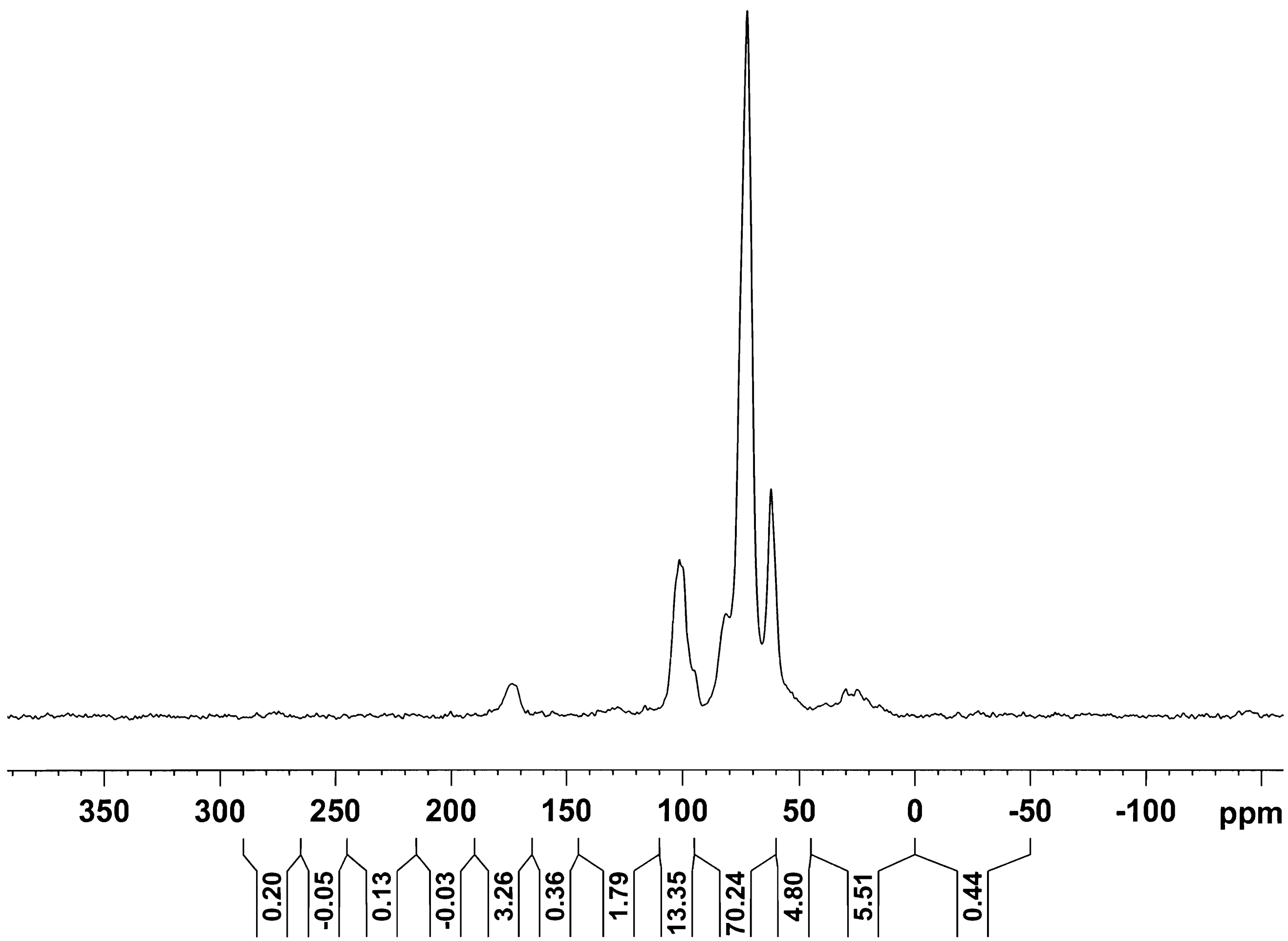


Current Data Parameters
NAME KBSNRate_Grain204_7A
EXPNO 1
PROCNO 1

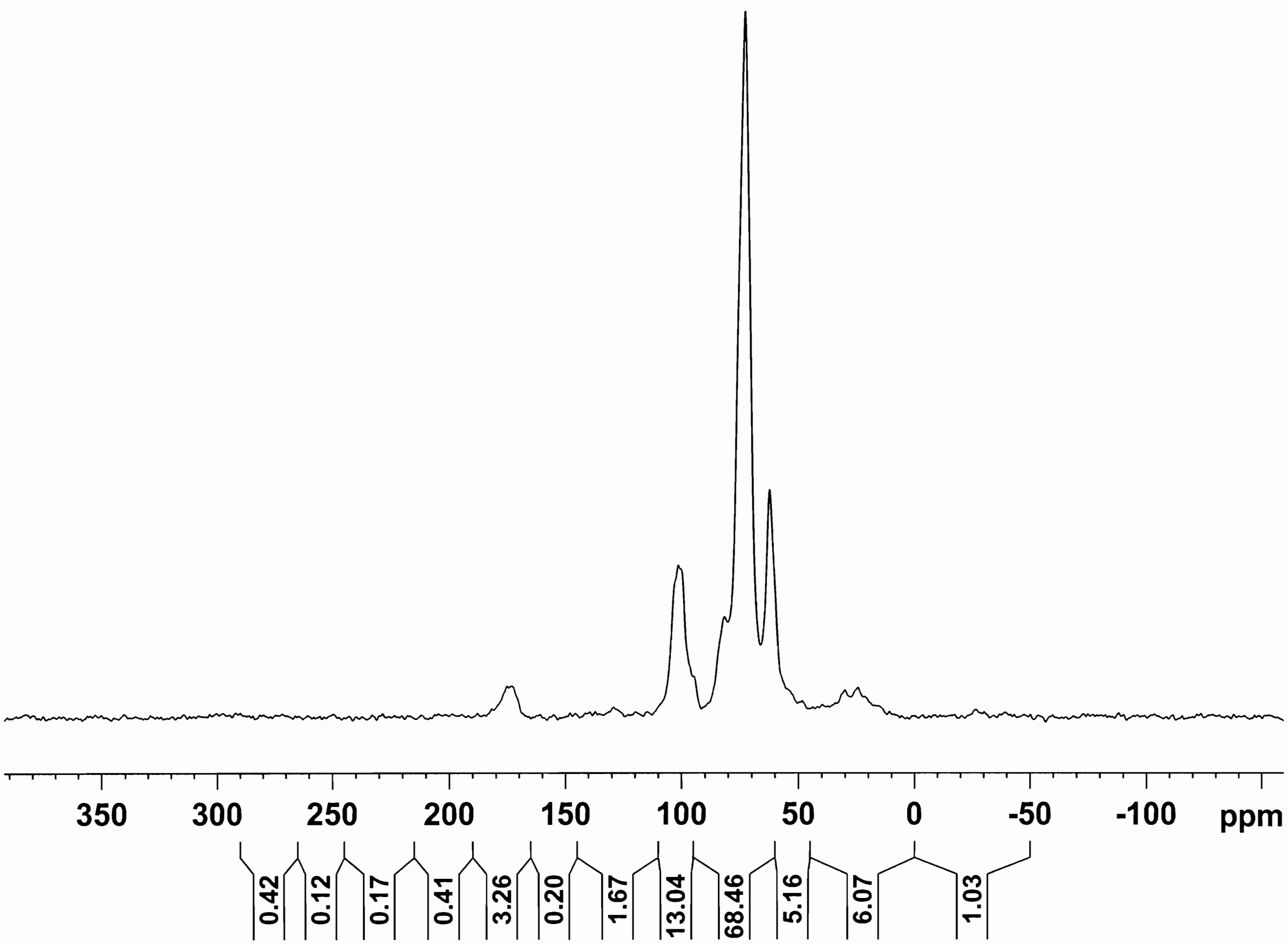
F2 - Acquisition Parameters
Date_ 20091127
Time 15.09
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7A Grain, Treatment 202 kg N/ha, Replicate 3, Cover Crop
11/27/2009 109.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain304_7A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091127
Time	16.07
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.1 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

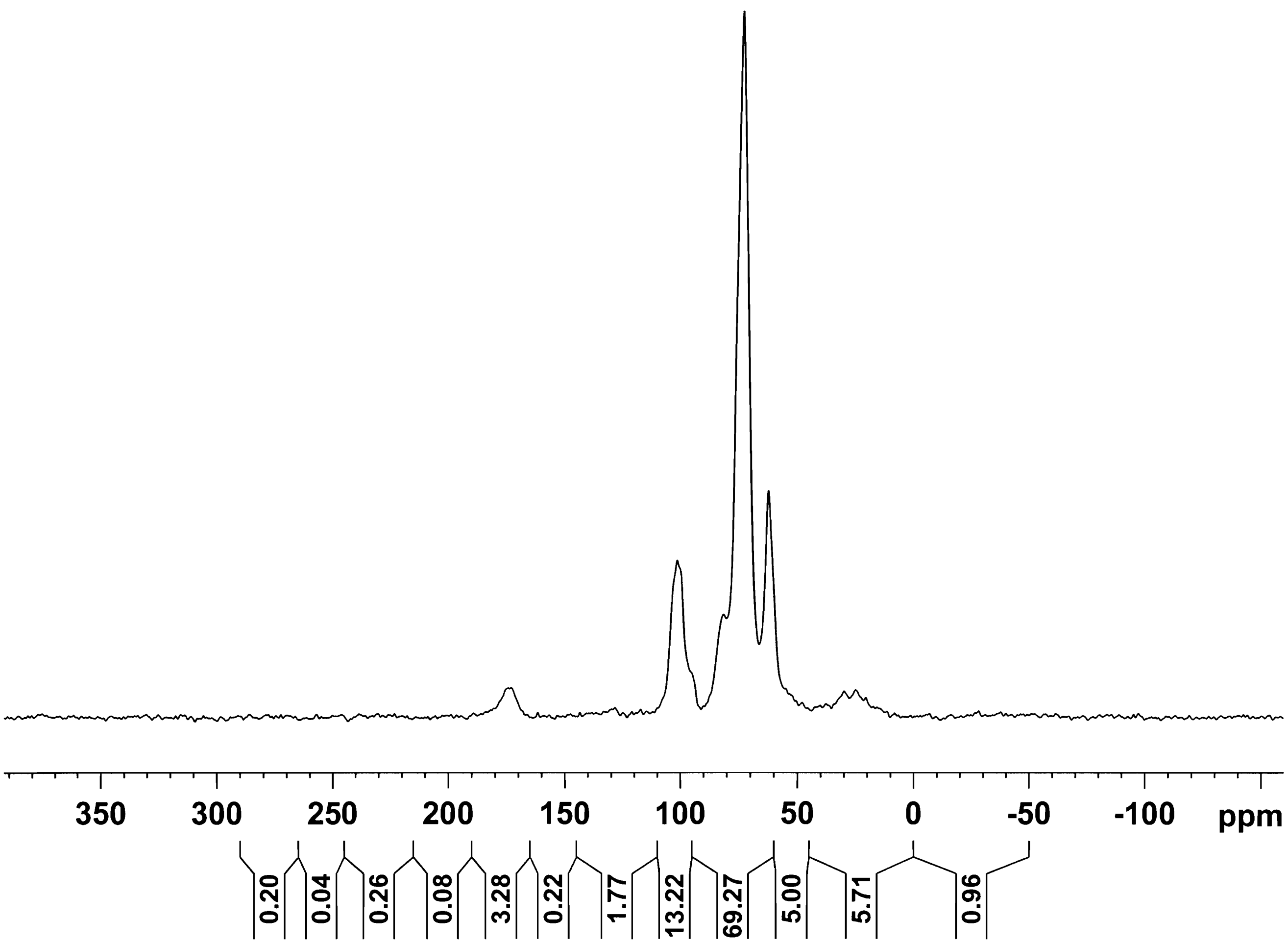
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7A Grain, Treatment 202 kg N/ha, Replicate 4, Cover Crop
11/27/2009   113.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters	
NAME	KBSNRate_Grain406_7A
EXPNO	1
PROCNO	1

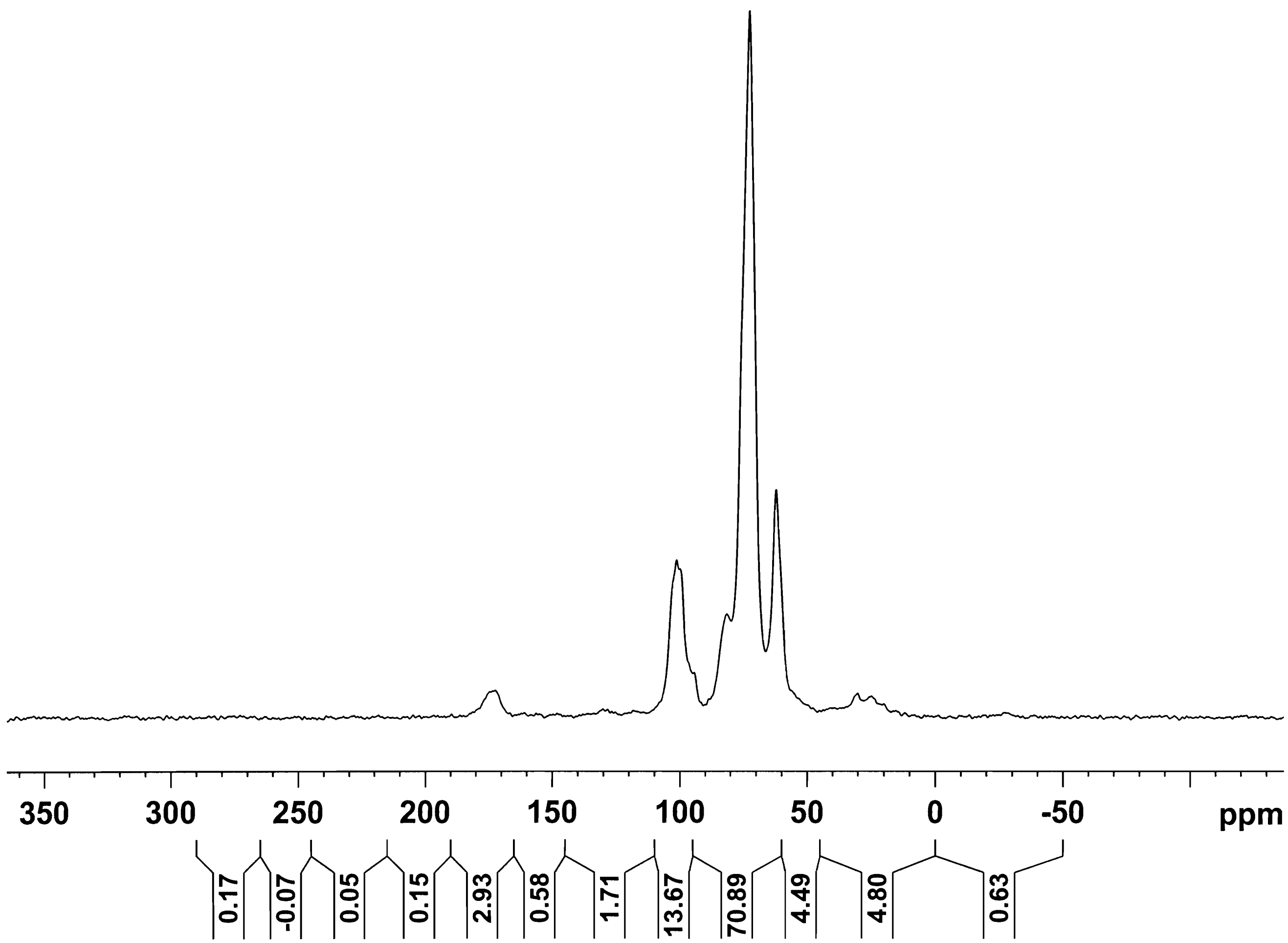
F2 - Acquisition Parameters	
Date_	20091127
Time	19.33
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.1 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========	
NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

======== CHANNEL f2 ========	
CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters	
SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Grain, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/13/2008   103.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_Grain101_1B
EXPNO   1
PROCNO   1

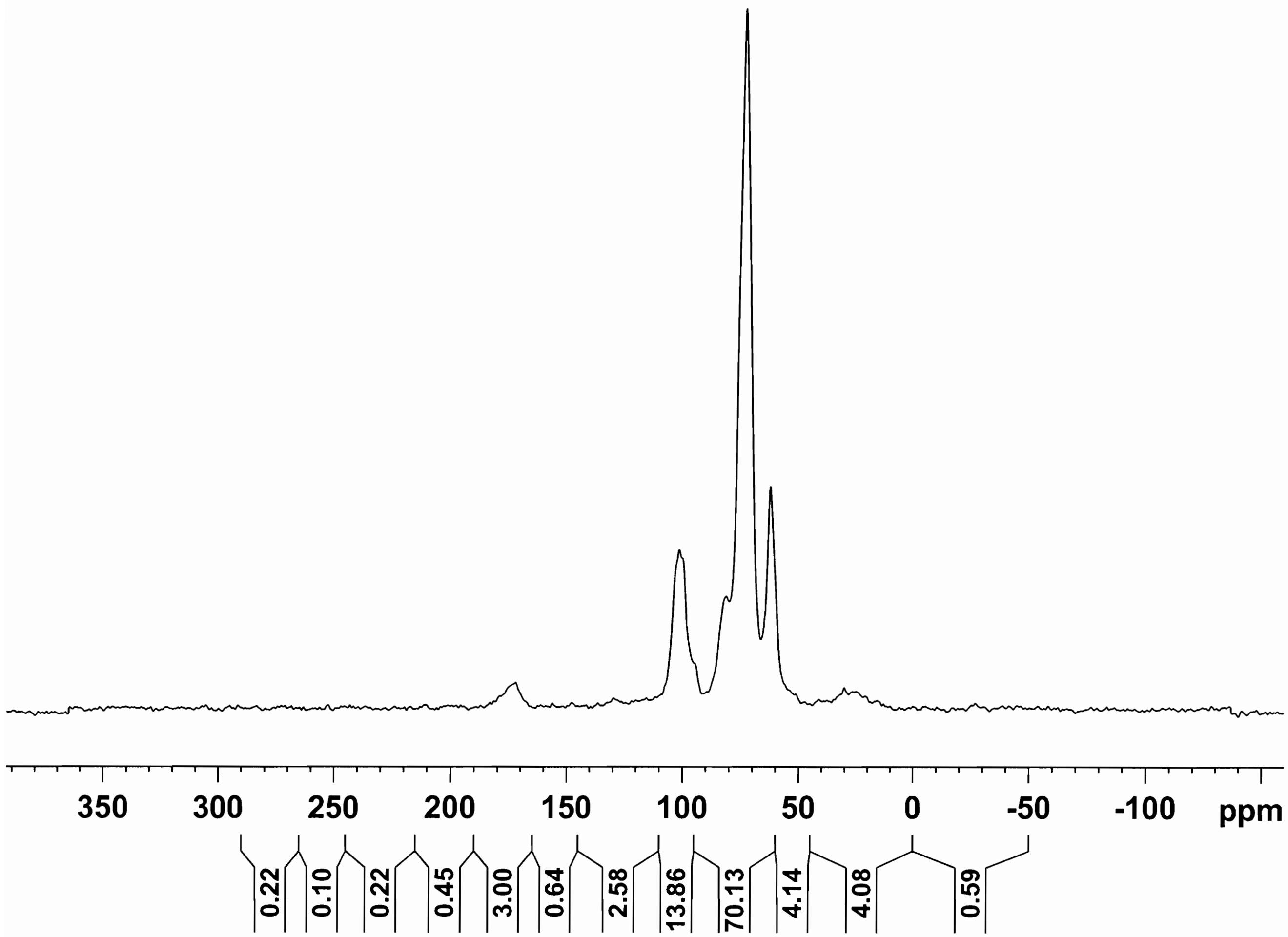
F2 - Acquisition Parameters
Date_   20080313
Time   19.30
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   7298.2
DW   19.800 usec
DE   6.00 usec
TE   698.0 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229662 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1B Grain, Treatment 0 kg N/ha, Replicate 2, No Cover Crop
11/11/2009   108.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_Grain203_1B
EXPNO 1
PROCNO 1

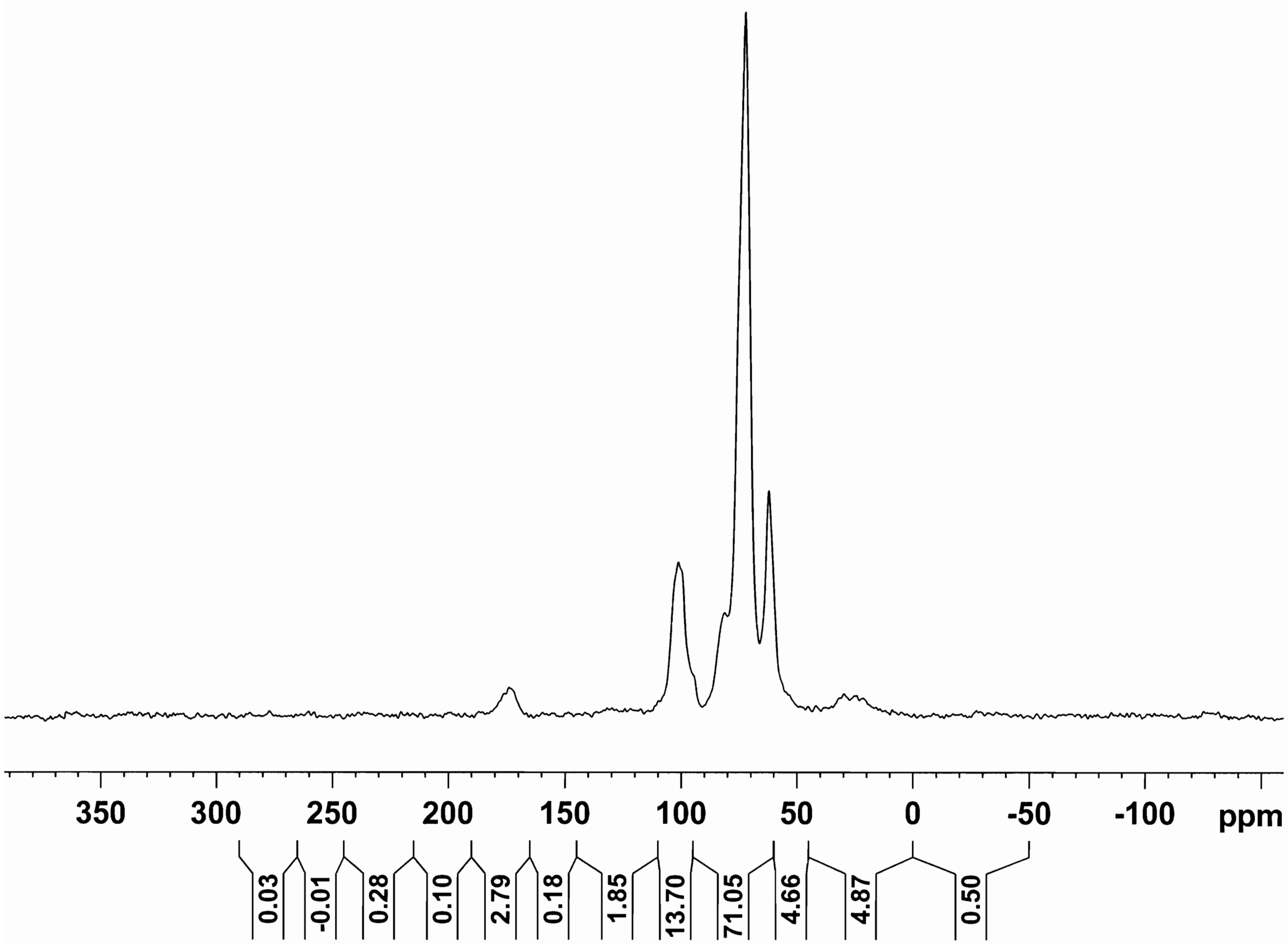
F2 - Acquisition Parameters
Date_ 20091111
Time 15.07
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1250
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 5

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1B Grain, Treatment 0 kg N/ha, Replicate 3, No Cover Crop
11/13/2009   112.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain307_1B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091113
Time	14.18
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	988
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.4 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

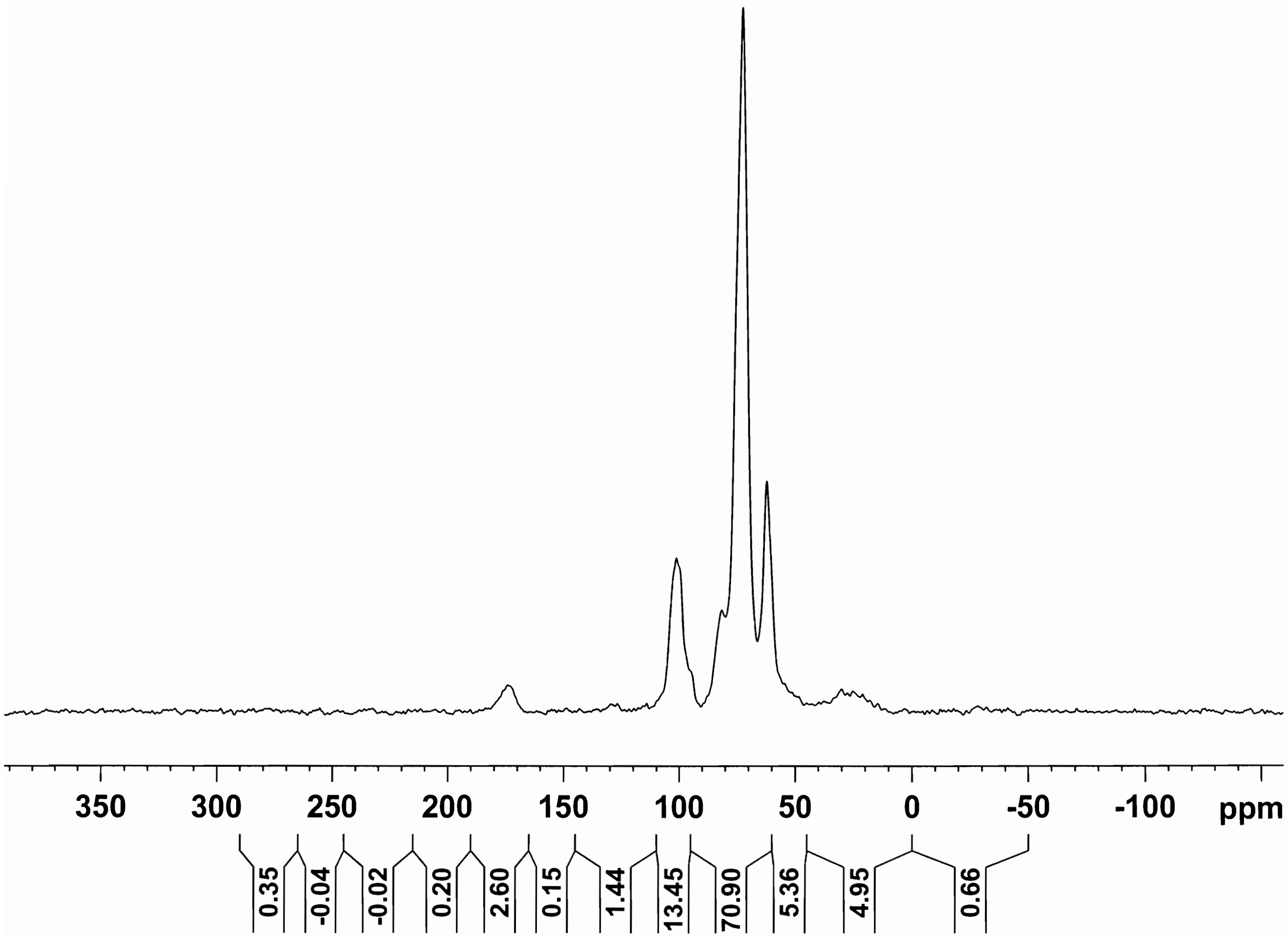
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1B Grain, Treatment 0 kg N/ha, Replicate 4, No Cover Crop
11/13/2009   106.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_Grain402_1B
EXPNO 1
PROCNO 1

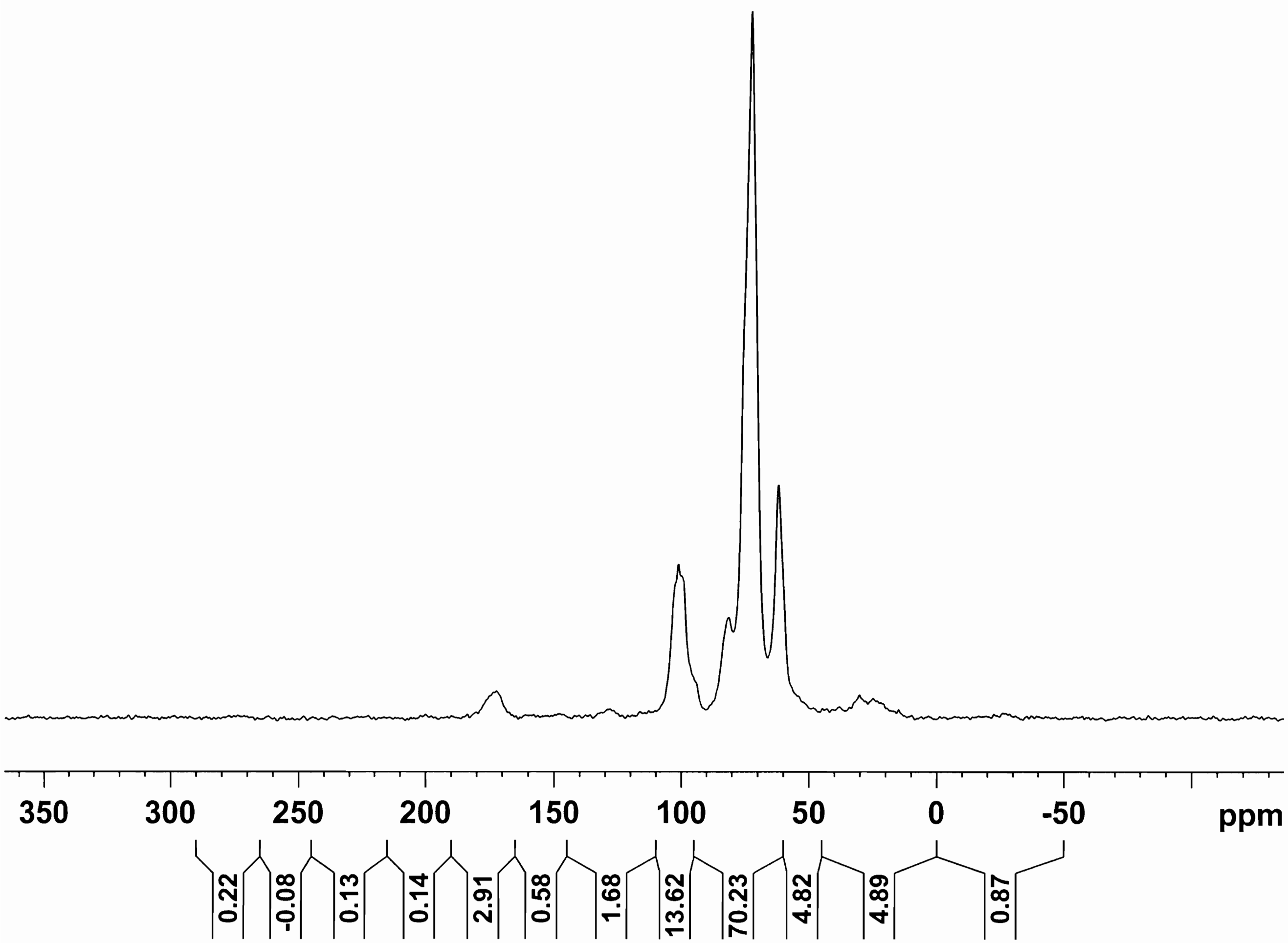
F2 - Acquisition Parameters
Date_ 20091113
Time 15.11
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Grain, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
10/26/2007   94.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_Grain107_2B
EXPNO                       1
PROCNO                      1

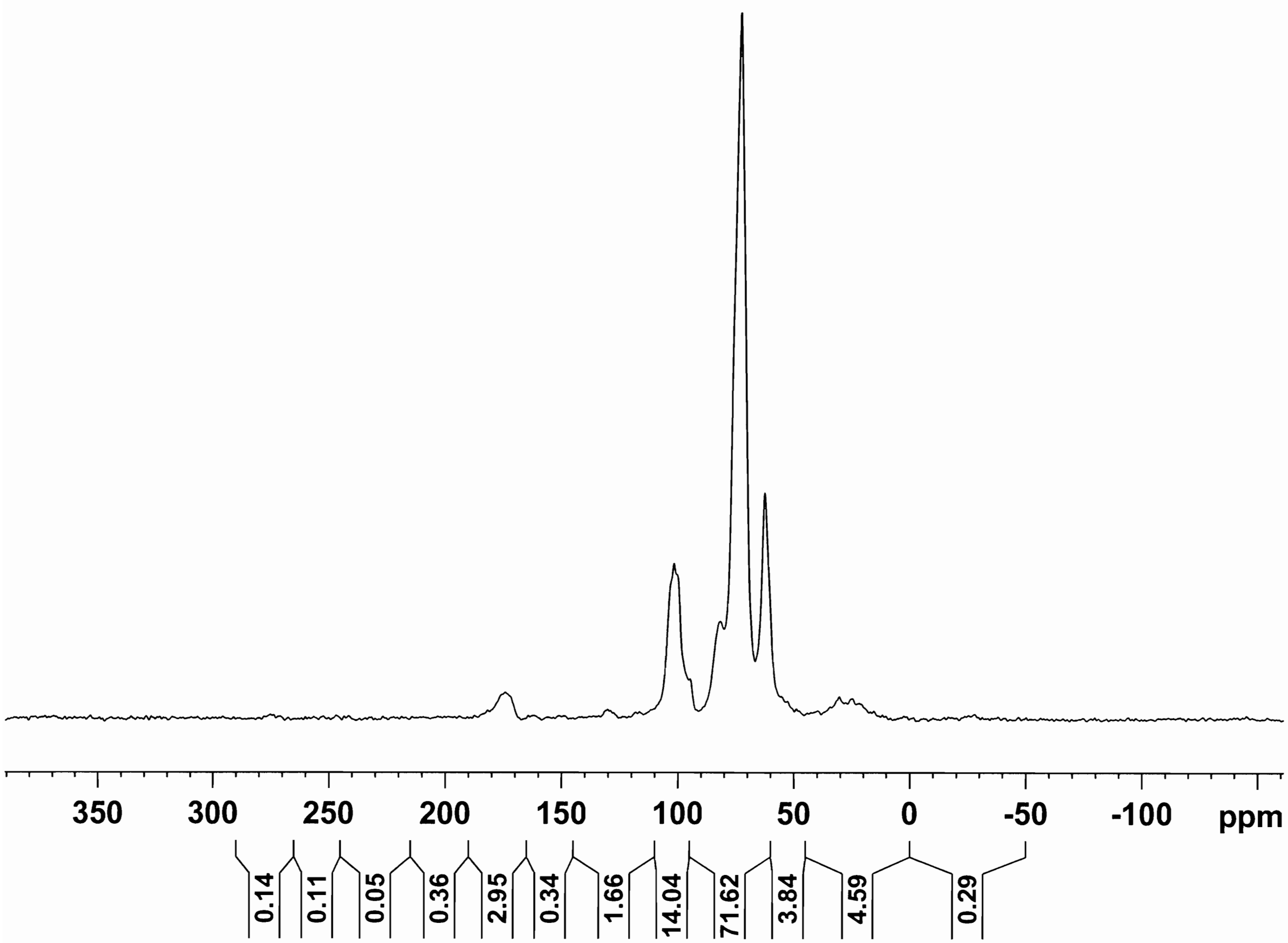
F2 - Acquisition Parameters
Date_            20071026
Time                13.52
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                 2580.3
DW                 19.800 usec
DE                   6.00 usec
TE                  698.2 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  1.40 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.10 usec
P31                  5.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229197 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Grain, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/16/2008   100.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_Grain106_3B
EXPNO                    1
PROCNO                   1

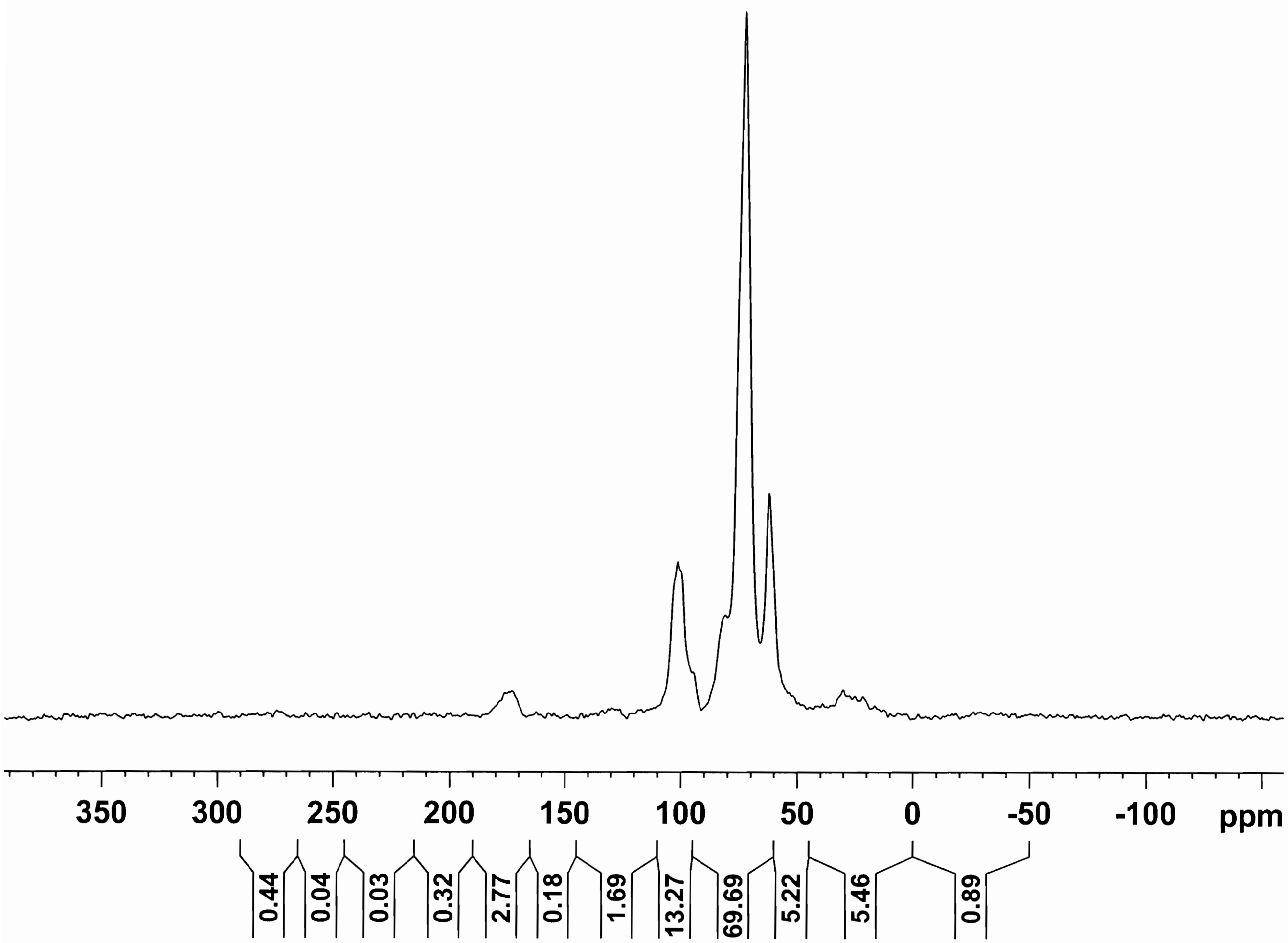
F2 - Acquisition Parameters
Date_             20080616
Time                 18.24
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG         cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                    6.00 usec
TE                   697.7 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.10 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229336 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3B Grain, Treatment 67 kg N/ha, Replicate 2, No Cover Crop
11/14/2009   107.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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```
Current Data Parameters
NAME     KBSNRate_Grain202_3B
EXPNO                       1
PROCNO                      1

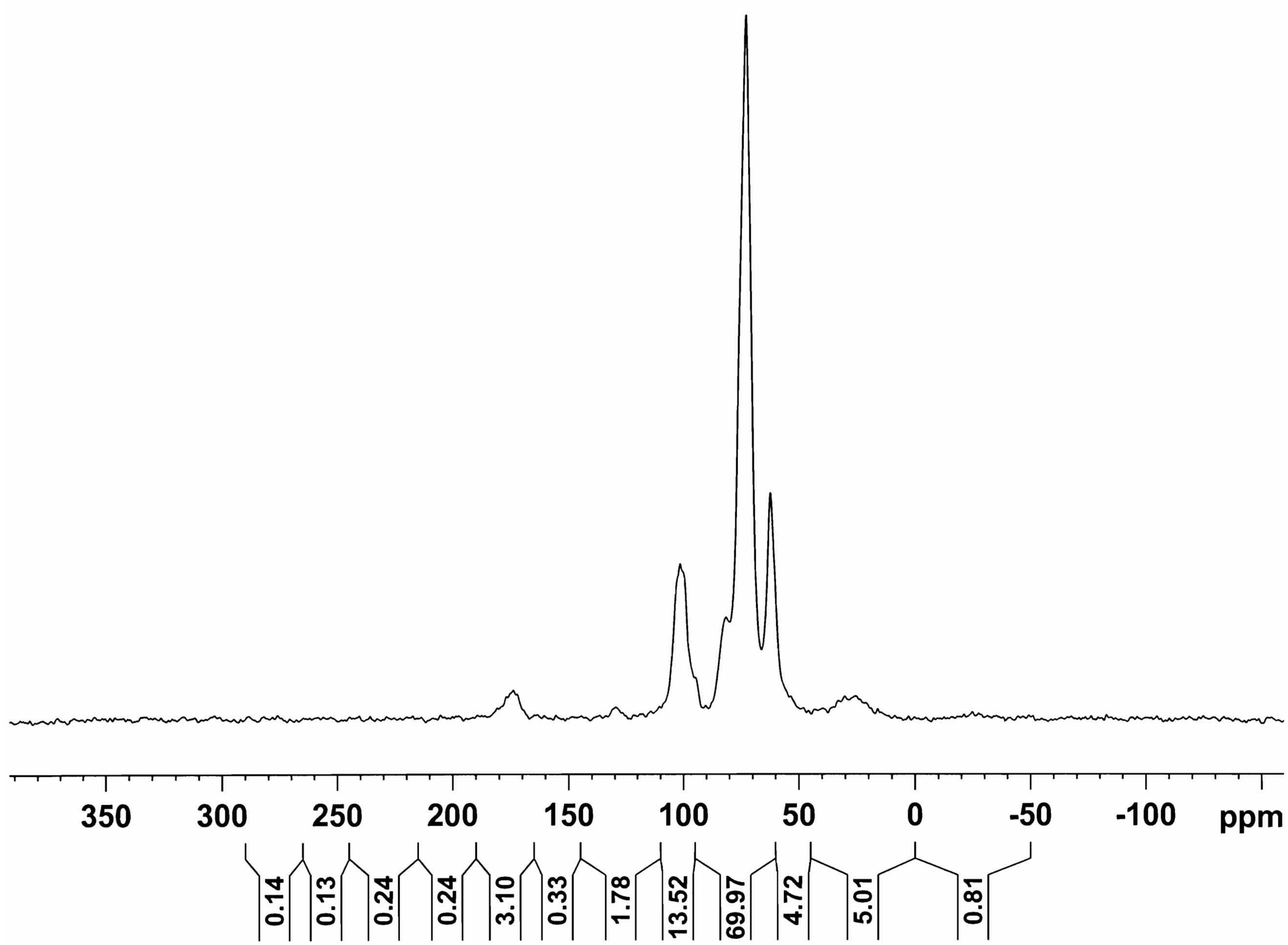
F2 - Acquisition Parameters
Date_            20091114
Time                20.25
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                   1024
SOLVENT
NS                   1000
DS                      0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                   2048
DW                 18.000 usec
DE                  17.00 usec
TE                  292.3 K
D1             3.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  2.40 dB
SFO1           50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.15 usec
P31                  6.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3228472 MHz
WDW                    EM
SSB                     0
LB                  40.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3B Grain, Treatment 67 kg N/ha, Replicate 3, No Cover Crop
11/15/2009   113.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_Grain305_3B
EXPNO                   1
PROCNO                  1

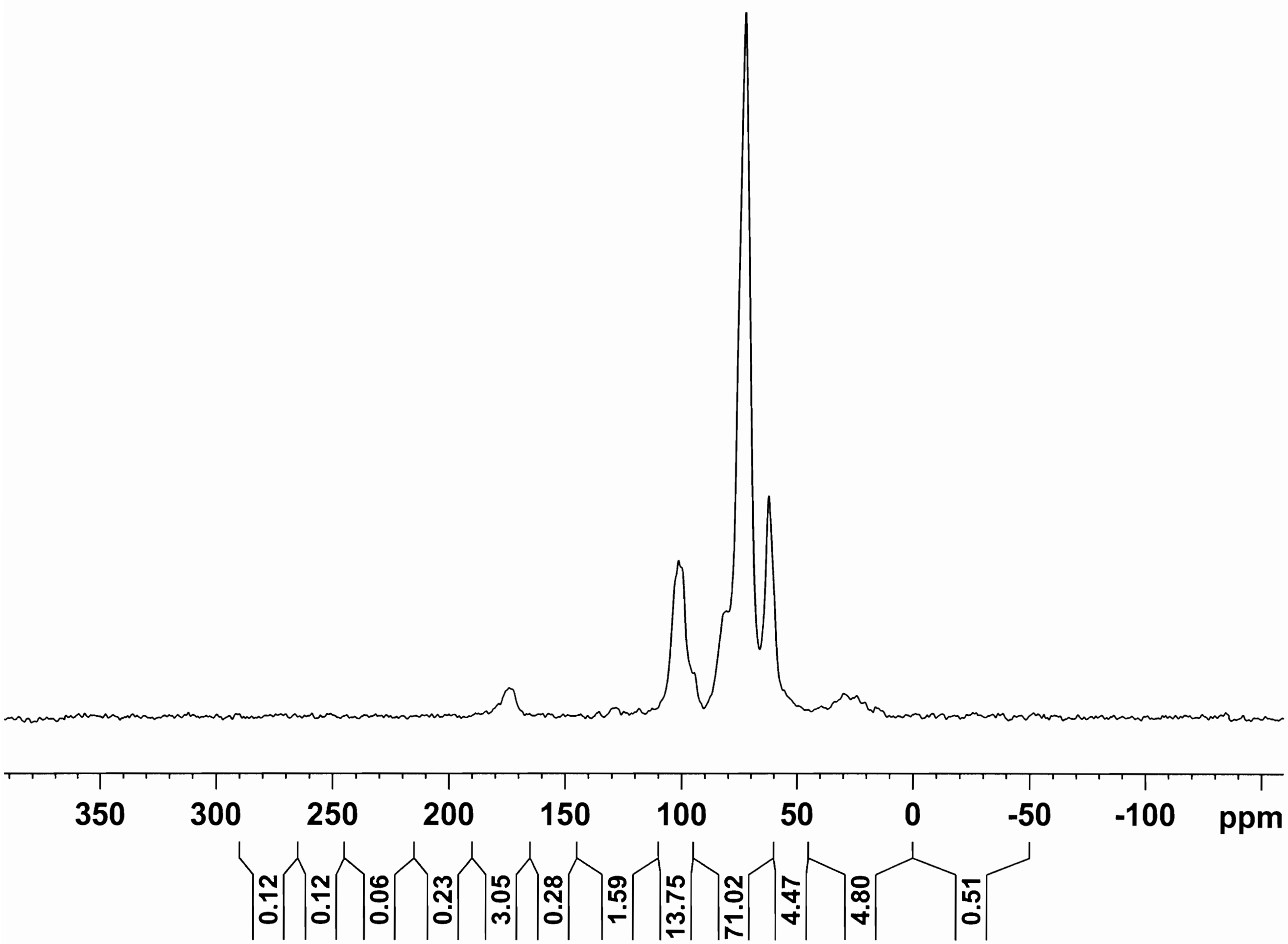
F2 - Acquisition Parameters
Date_          20091115
Time              11.48
INSTRUM           spect
PROBHD   4 mm MASxvt BB
PULPROG       cp.99.WCH
TD                 1024
SOLVENT
NS                 1000
DS                    0
SWH          27777.777 Hz
FIDRES       27.126736 Hz
AQ           0.0185000 sec
RG                 2048
DW              18.000 usec
DE               17.00 usec
TE               292.3 K
D1          3.00000000 sec
TD0                   4

======== CHANNEL f1 ========
NUC1                13C
P15             1000.00 usec
PL1                2.40 dB
SFO1         50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2          tppm15
NUC2                 1H
P3                 3.15 usec
P31                6.00 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                16384
SF           50.3228472 MHz
WDW                  EM
SSB                   0
LB                40.00 Hz
GB                    0
PC                 1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3B Grain, Treatment 67 kg N/ha, Replicate 4, No Cover Crop
11/15/2009   111.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain404_3B	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20091115	
Time	12.44	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	292.4	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

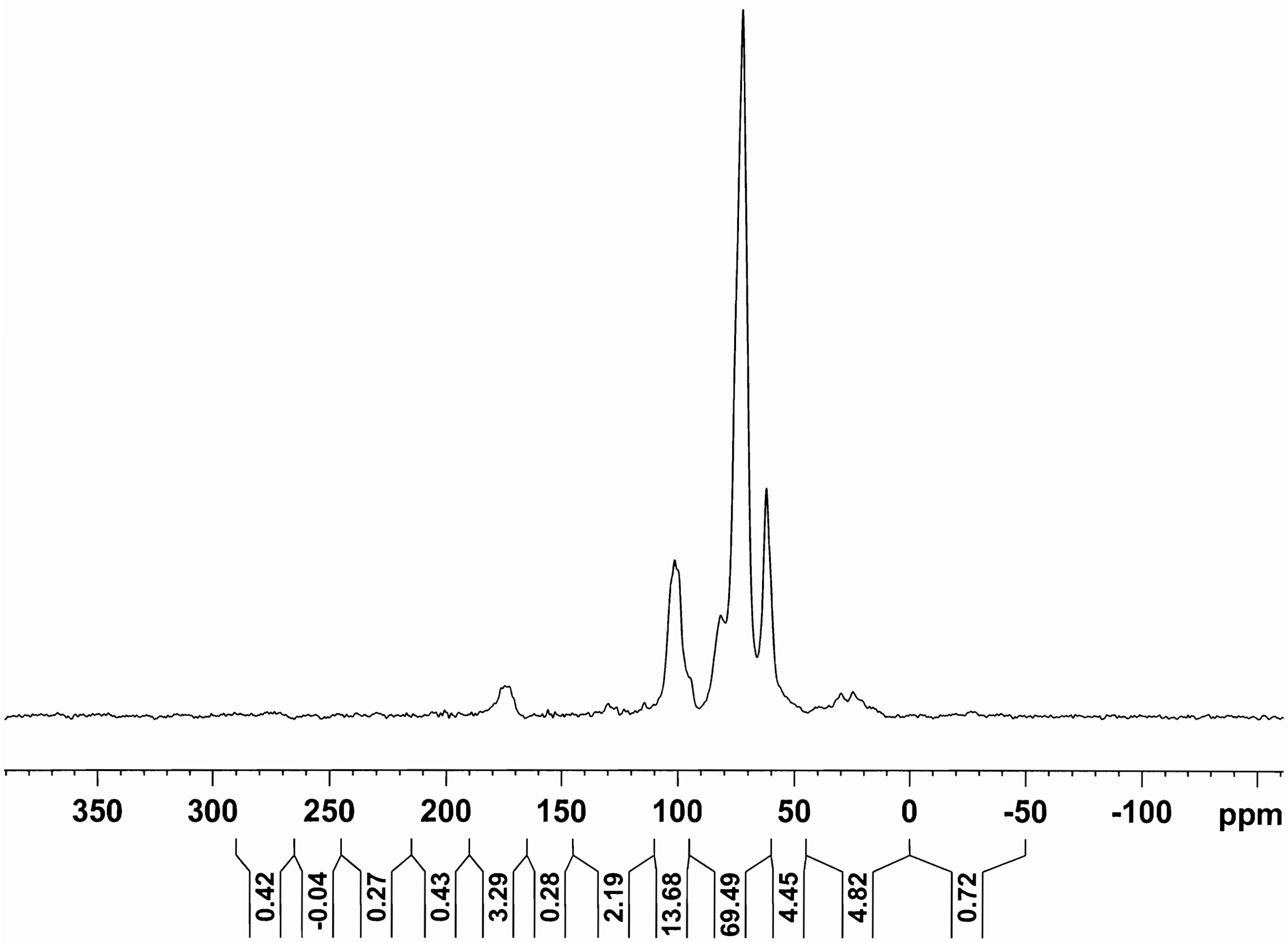
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Grain, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/14/2008   105.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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```
Current Data Parameters
NAME      KBSNRate_Grain102_4B
EXPNO                        1
PROCNO                       1

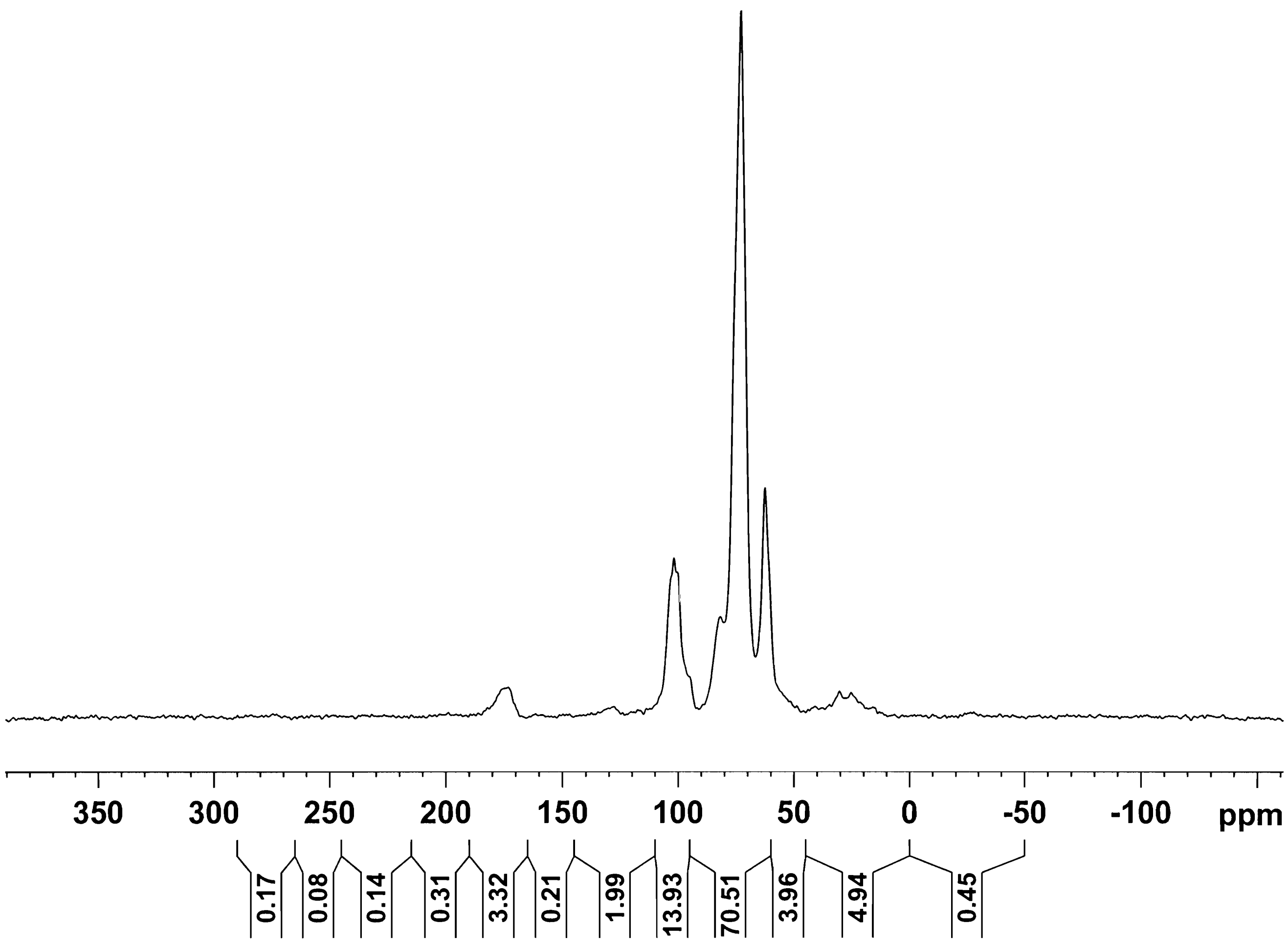
F2 - Acquisition Parameters
Date_             20080614
Time                 10.27
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                 3649.1
DW                 18.000 usec
DE                   6.00 usec
TE                  697.5 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15               1000.00 usec
PL1                  1.40 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                   3.10 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

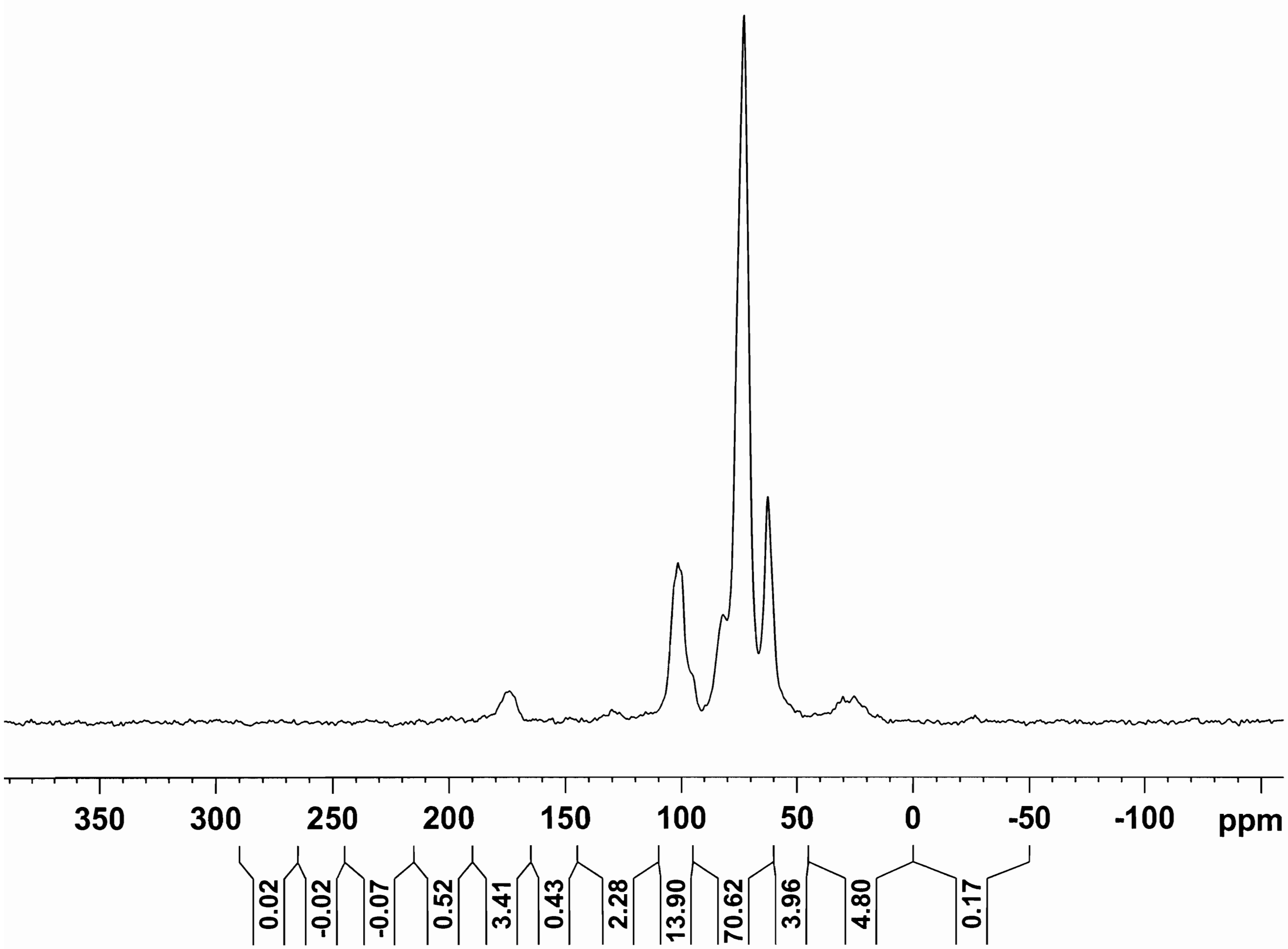
F2 - Processing parameters
SI                   16384
SF              50.3229336 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Grain, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/12/2008   100.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters		
NAME	KBSNRate_Grain104_5B	
EXPNO	1	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20080612	
Time	15.47	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	3649.1	
DW	18.000	usec
DE	6.00	usec
TE	698.4	K
D1	2.00000000	sec
======== CHANNEL f1 ========		
NUC1	13C	
P15	1000.00	usec
PL1	1.40	dB
SFO1	50.3287071	MHz
======== CHANNEL f2 ========		
CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.10	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz
F2 - Processing parameters		
SI	16384	
SF	50.3229336	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5B Grain, Treatment 134 kg N/ha, Replicate 2, No Cover Crop
01/03/2010   107.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain205_5B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100103
Time	12.07
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	291.7 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

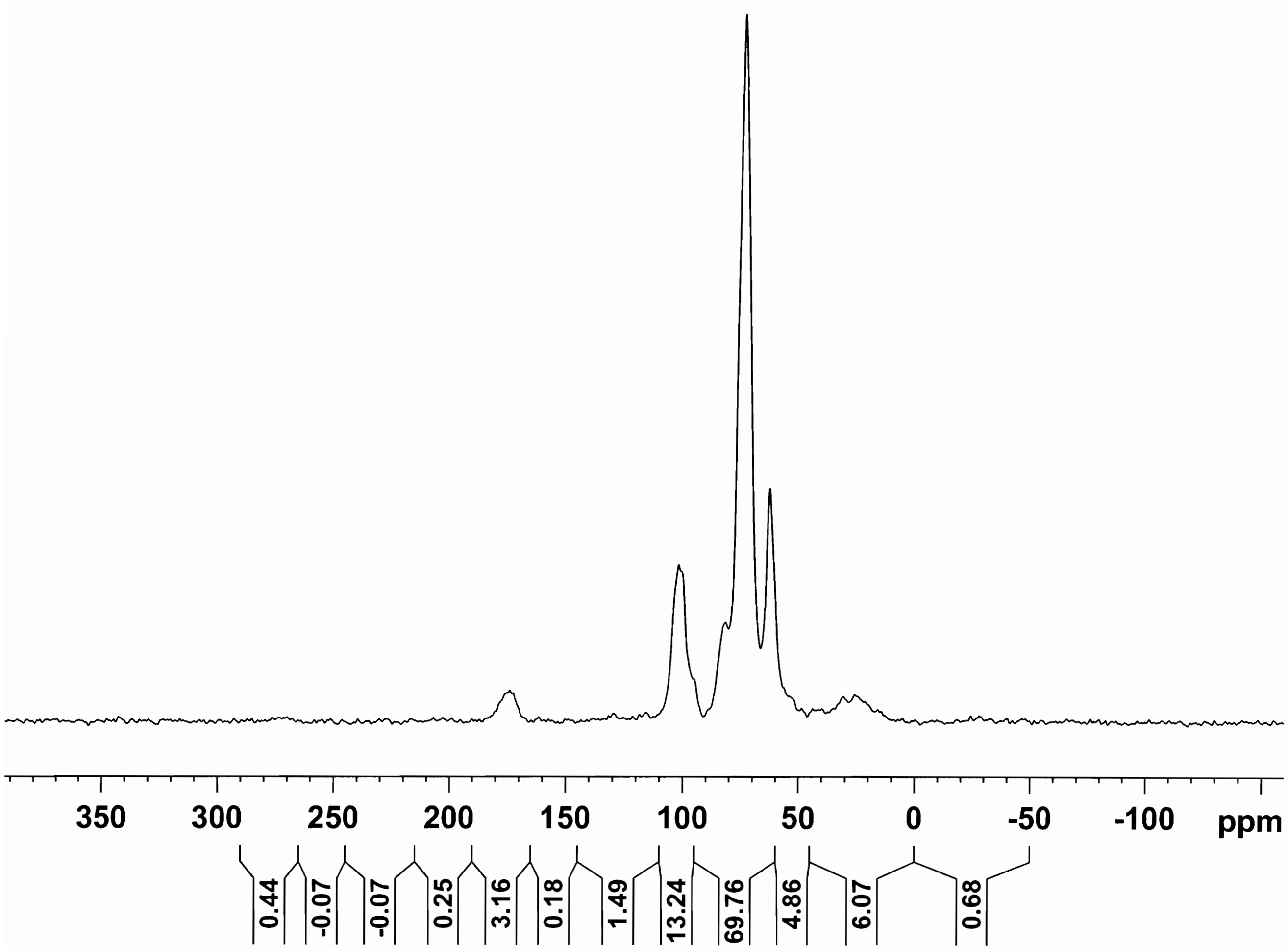
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5B Grain, Treatment 134 kg N/ha, Replicate 3, No Cover Crop
01/03/2010   111.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain302_5B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100103	
Time	13.06	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	291.8	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

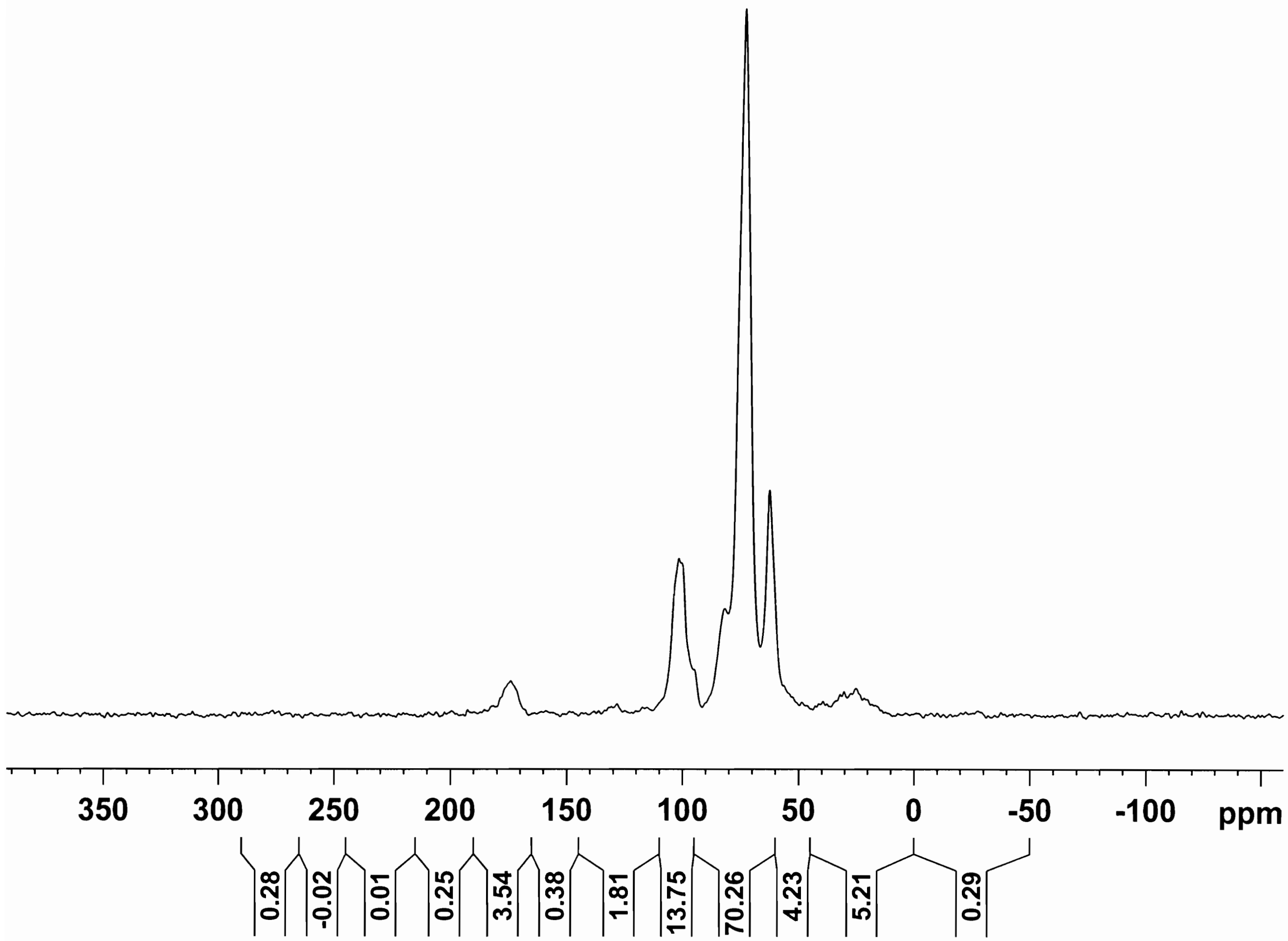
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5B Grain, Treatment 134 kg N/ha, Replicate 4, No Cover Crop
01/03/2010 113.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain407_5B	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20100103	
Time	14.04	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	291.9	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

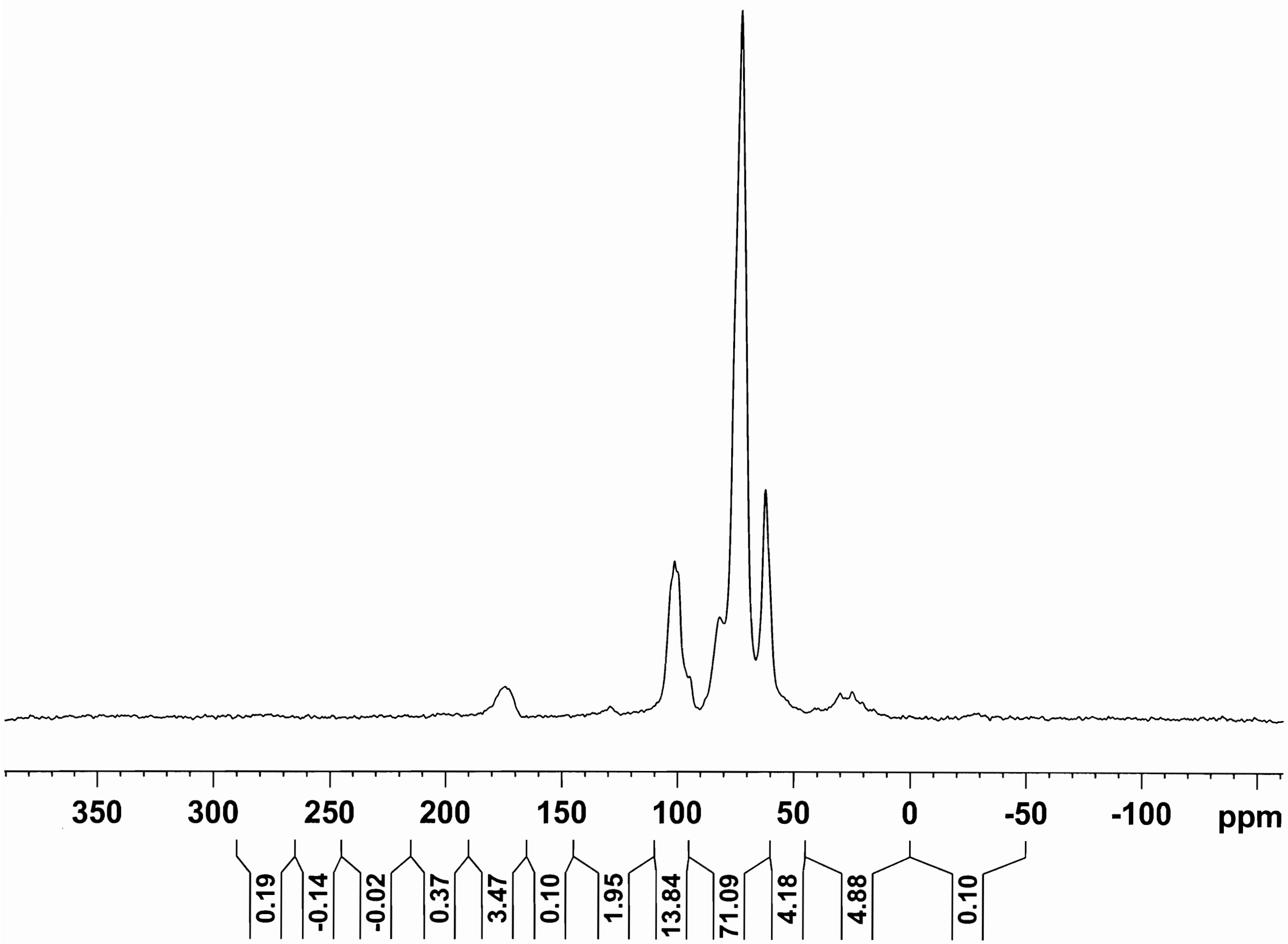
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Grain, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/11/2008   102.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_Grain103_6B
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20080611
Time                21.03
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                 3649.1
DW                 18.000 usec
DE                   6.00 usec
TE                  698.2 K
D1             2.00000000 sec

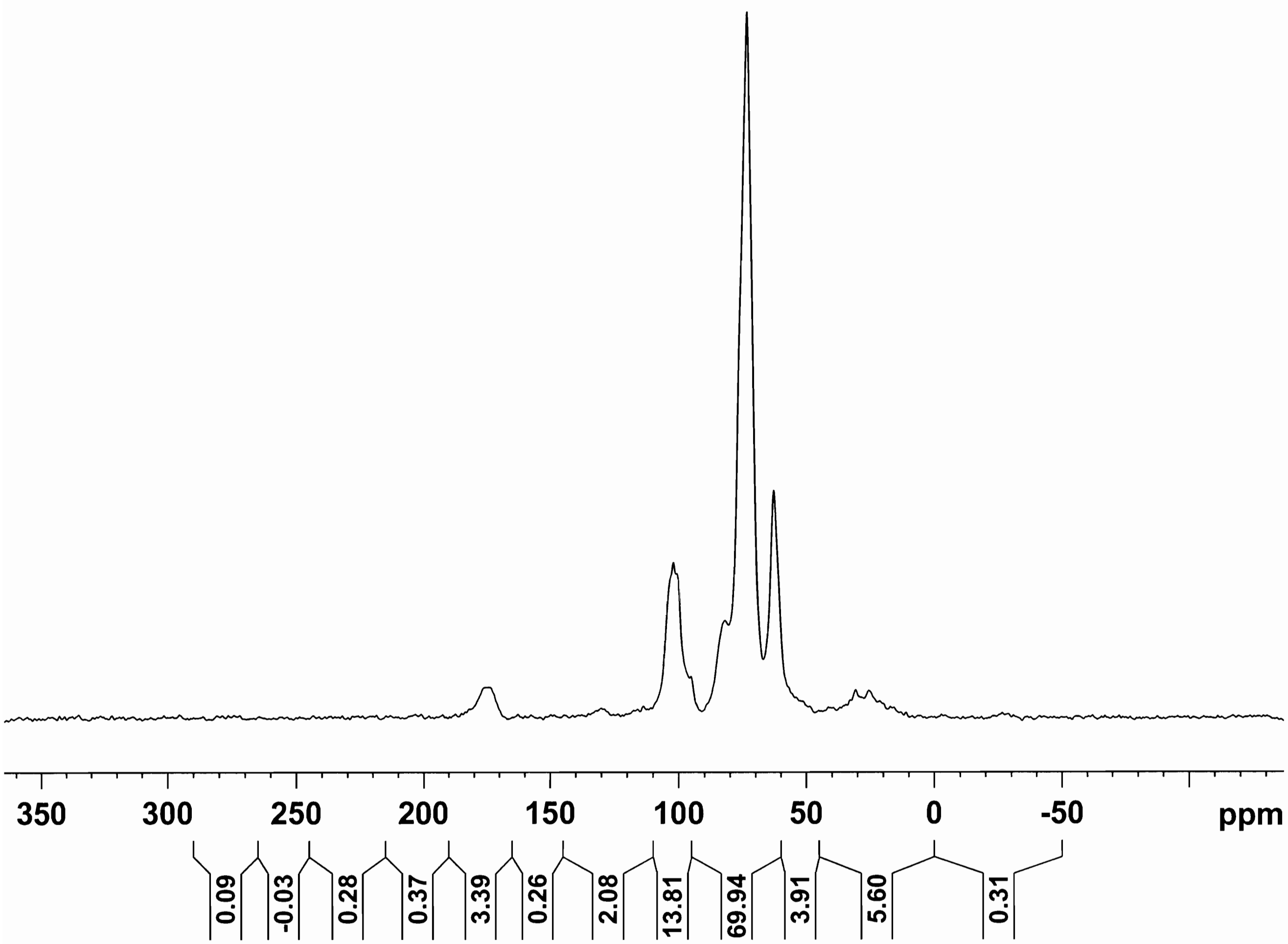
======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  1.40 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.10 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229336 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

324

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Grain, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/14/2008   103.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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```
Current Data Parameters
NAME     KBSNRate_Grain105_7B
EXPNO                       1
PROCNO                      1

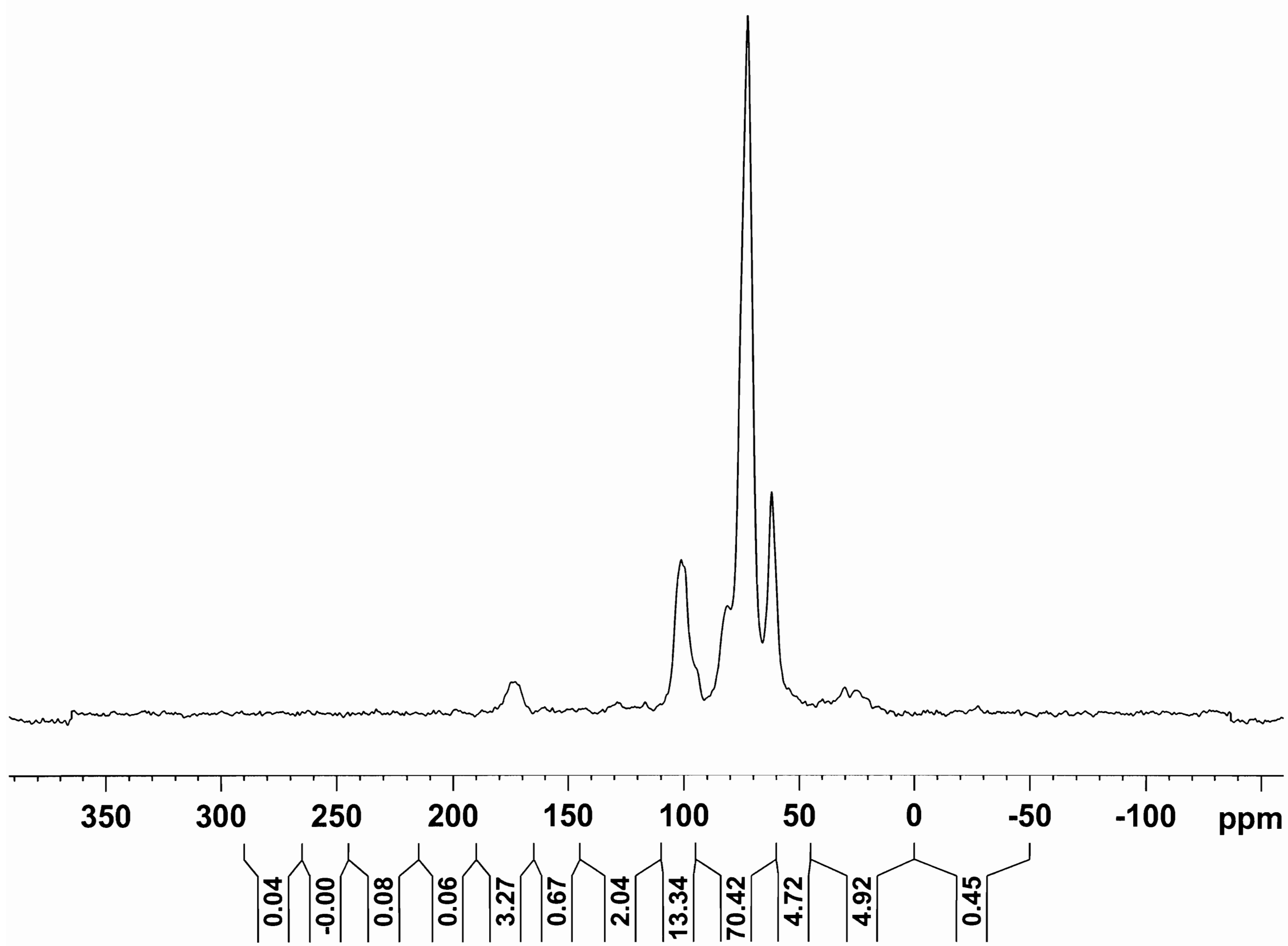
F2 - Acquisition Parameters
Date_            20080314
Time                12.14
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                  724.1
DW                 19.800 usec
DE                   6.00 usec
TE                  694.6 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  1.40 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.05 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229662 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7B Grain, Treatment 202 kg N/ha, Replicate 2, No Cover Crop
11/11/2009   106.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

Current Data Parameters
NAME KBSNRate_Grain204_7B
EXPNO 1
PROCNO 1

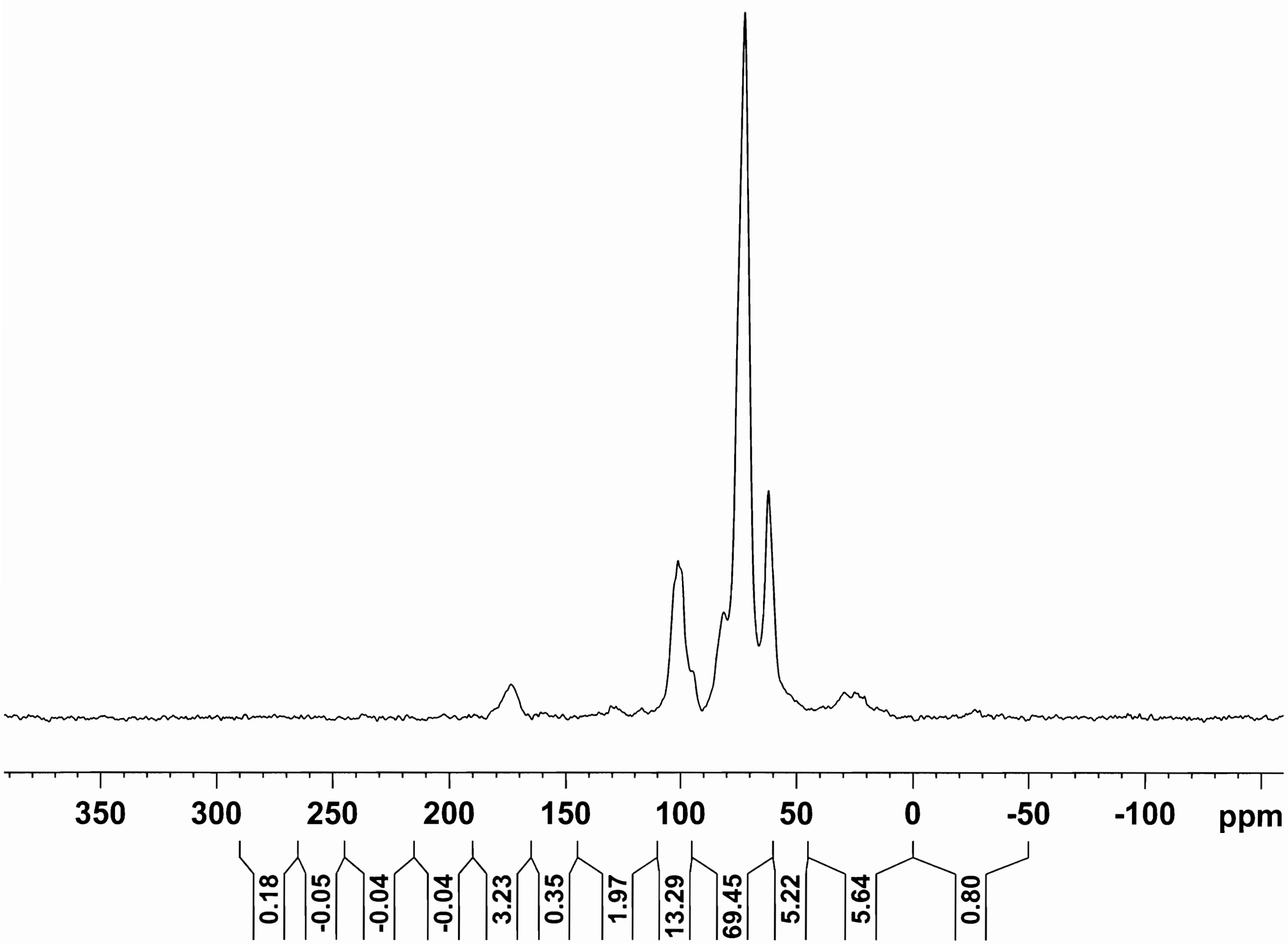
F2 - Acquisition Parameters
Date_ 20091111
Time 13.04
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7B Grain, Treatment 202 kg N/ha, Replicate 3, No Cover Crop
11/13/2009   112.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_Grain304_7B
EXPNO 1
PROCNO 1

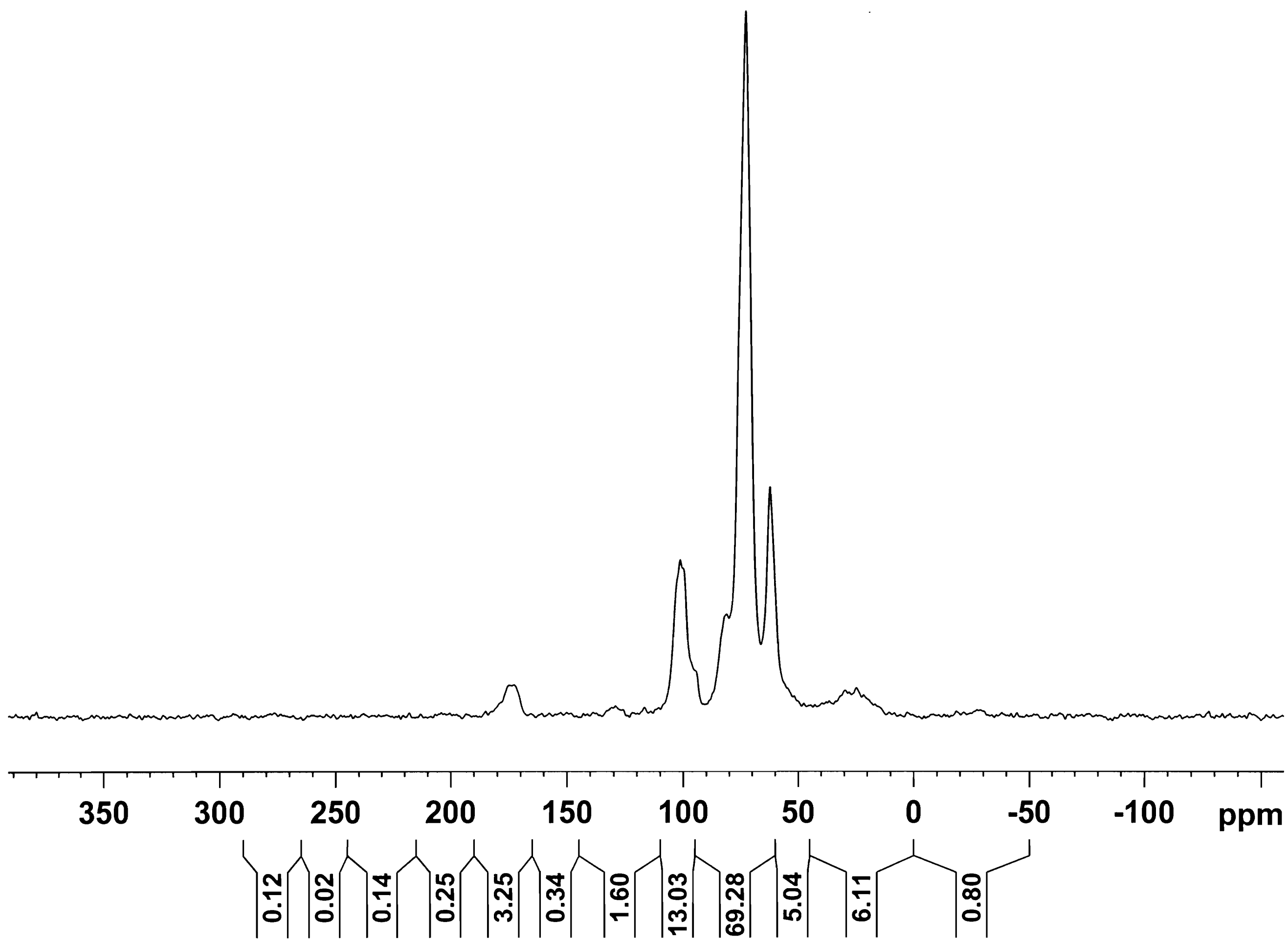
F2 - Acquisition Parameters
Date_ 20091113
Time 13.10
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7B Grain, Treatment 202 kg N/ha, Replicate 4, No Cover Crop
11/13/2009   111.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_Grain406_7B	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20091113	
Time	16.09	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	292.4	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

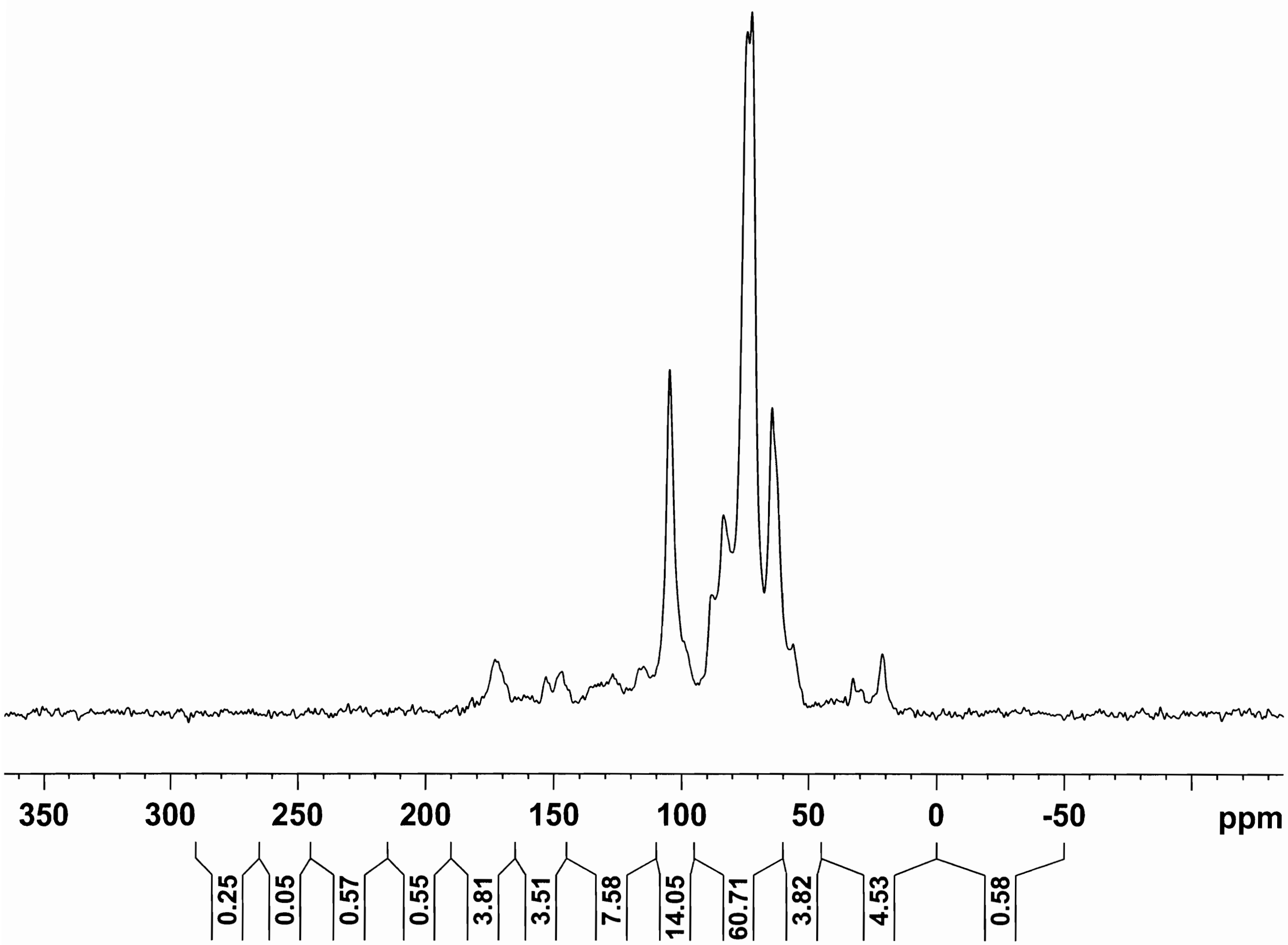
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, Cover Crop
10/26/2007   56.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_LS101_1A
EXPNO   1
PROCNO   1

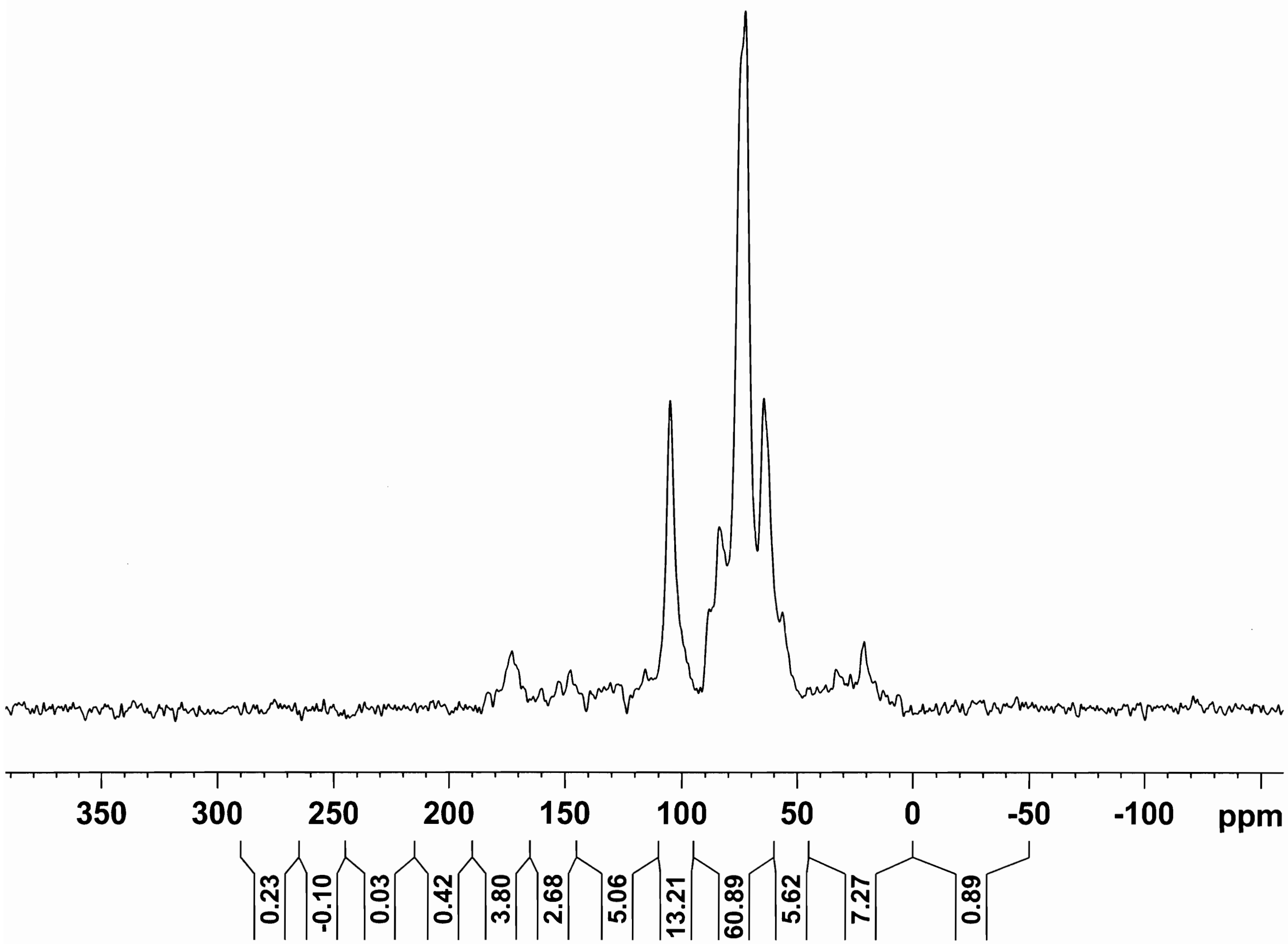
F2 - Acquisition Parameters
Date_   20071026
Time   16.41
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   1625.5
DW   19.800 usec
DE   6.00 usec
TE   698.2 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.10 usec
P31   5.00 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229197 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 2, Cover Crop
11/28/2009   62.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_LS203_1A
EXPNO   1
PROCNO   1

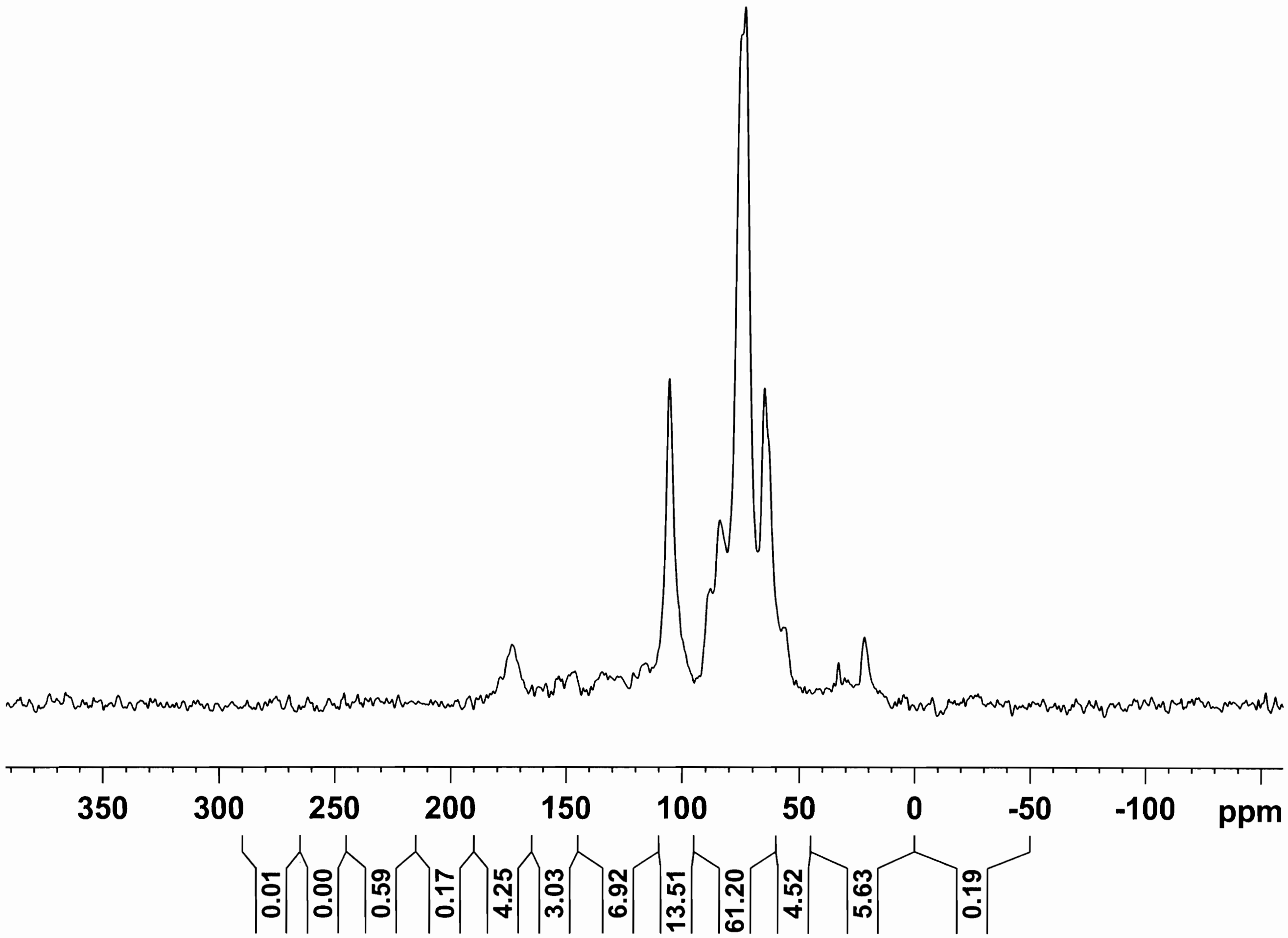
F2 - Acquisition Parameters
Date_   20091128
Time   19.46
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.WCH
TD   1024
SOLVENT
NS   1000
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   292.2 K
D1   3.00000000 sec
TD0   4

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.40 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.15 usec
P31   6.00 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228472 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 3, Cover Crop
12/30/2009   63.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_LS307_1A
EXPNO 1
PROCNO 1

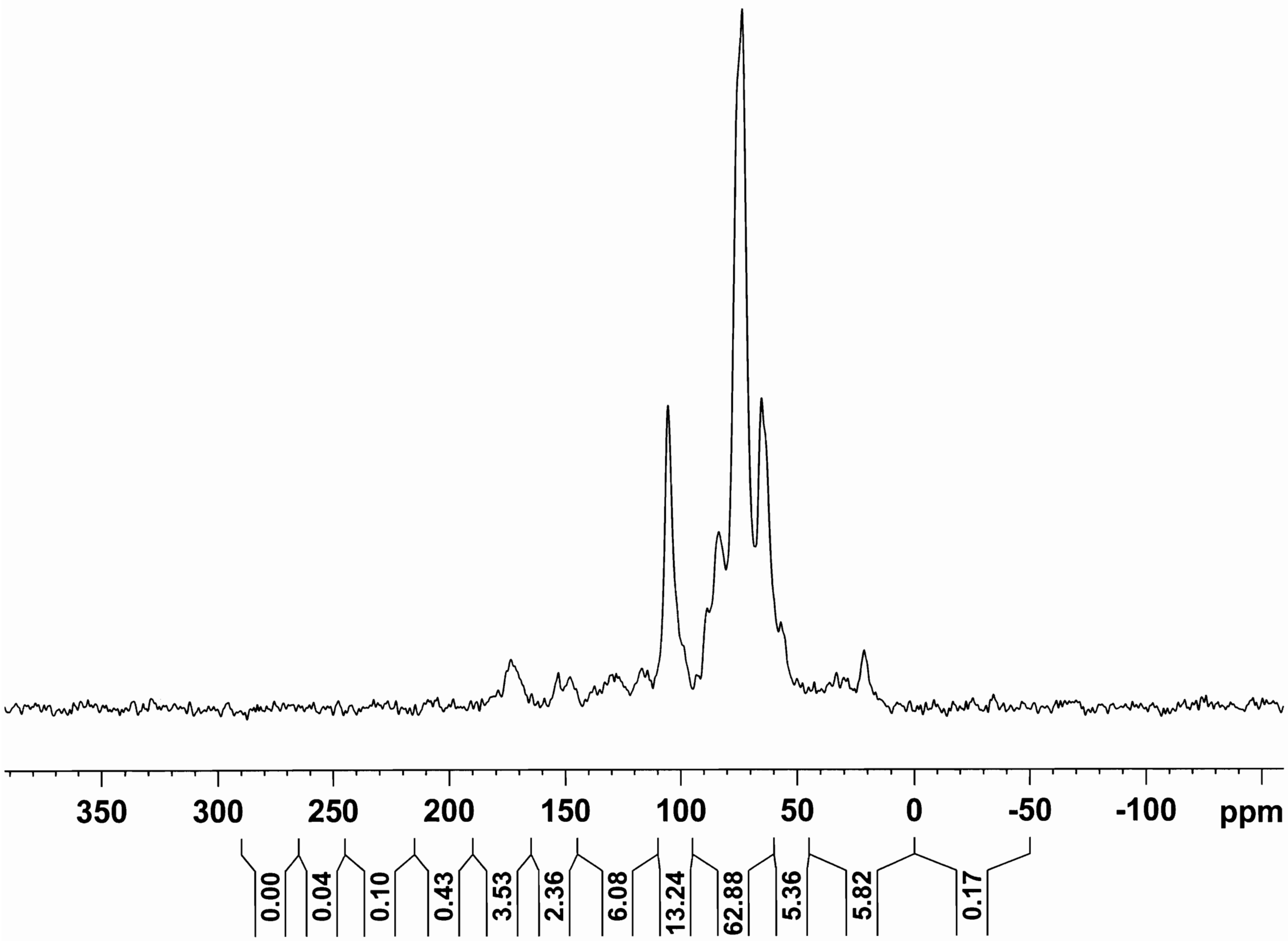
F2 - Acquisition Parameters
Date_ 20091230
Time 12.34
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 291.9 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 4, Cover Crop
12/30/2009   62.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_LS402_1A
EXPNO                    1
PROCNO                   1

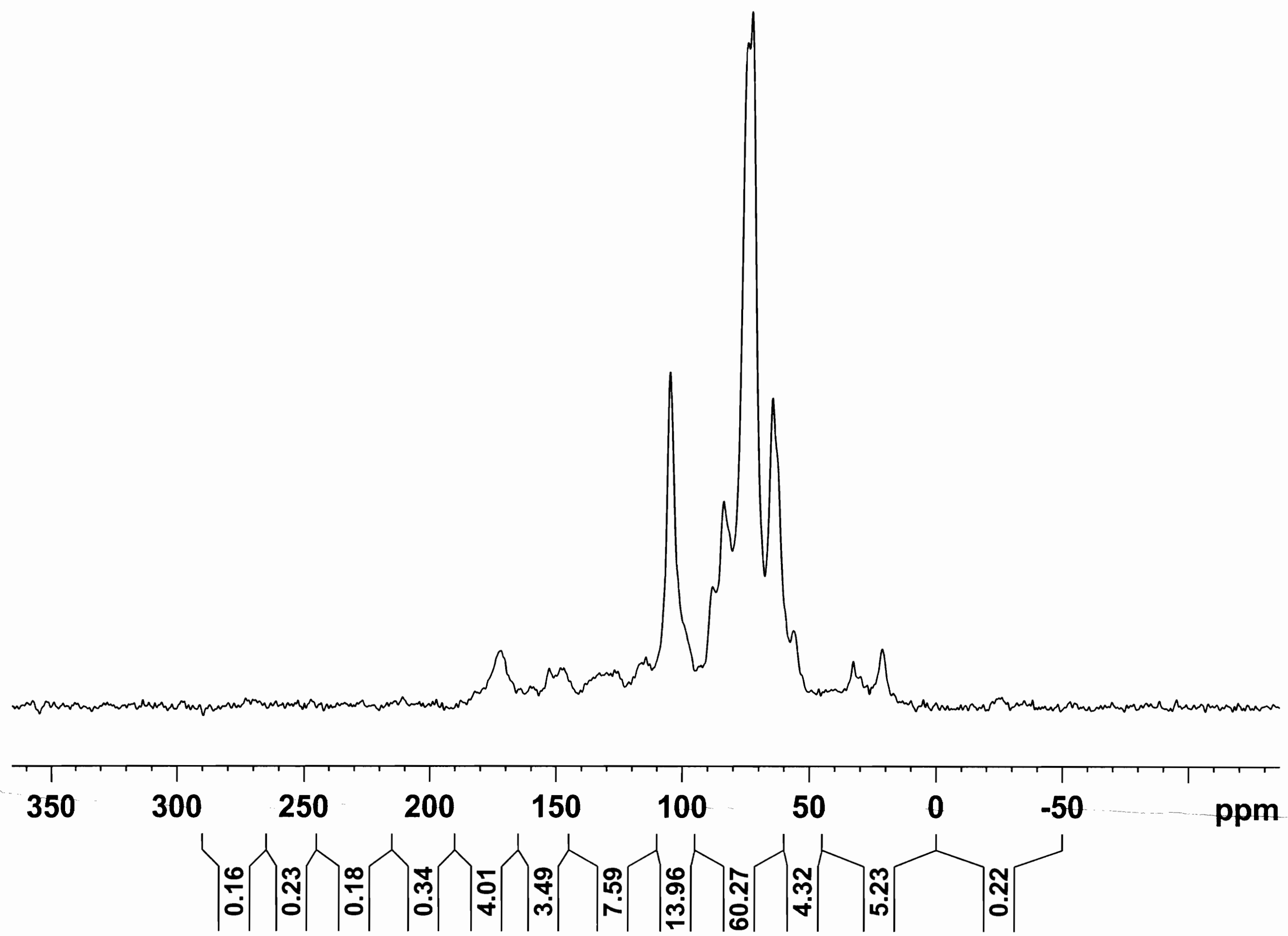
F2 - Acquisition Parameters
Date_             20091230
Time                 13.33
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   291.9 K
D1              3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, Cover Crop
10/27/2007   62.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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```
Current Data Parameters
NAME       KBSNRate_LS107_2A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071027
Time                  14.10
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG           cp.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                   1625.5
DW                   19.800 usec
DE                     6.00 usec
TE                    698.2 K
D1               2.00000000 sec

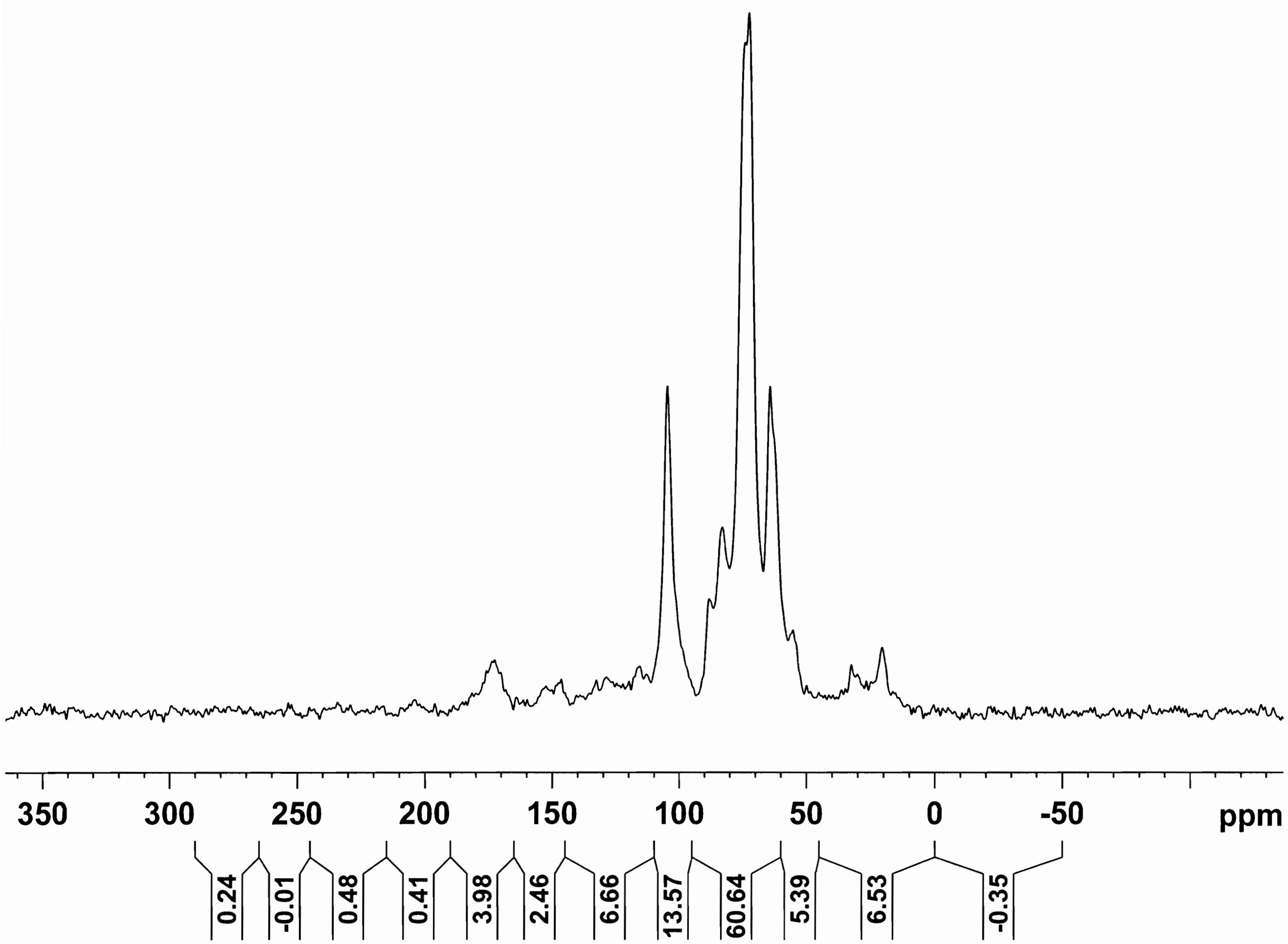
======== CHANNEL f1 ========
NUC1                    13C
P15                 1000.00 usec
PL1                    1.40 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.10 usec
P31                    5.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229197 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

333

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/07/2008 50.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_LS106_3A
EXPNO                    1
PROCNO                   1

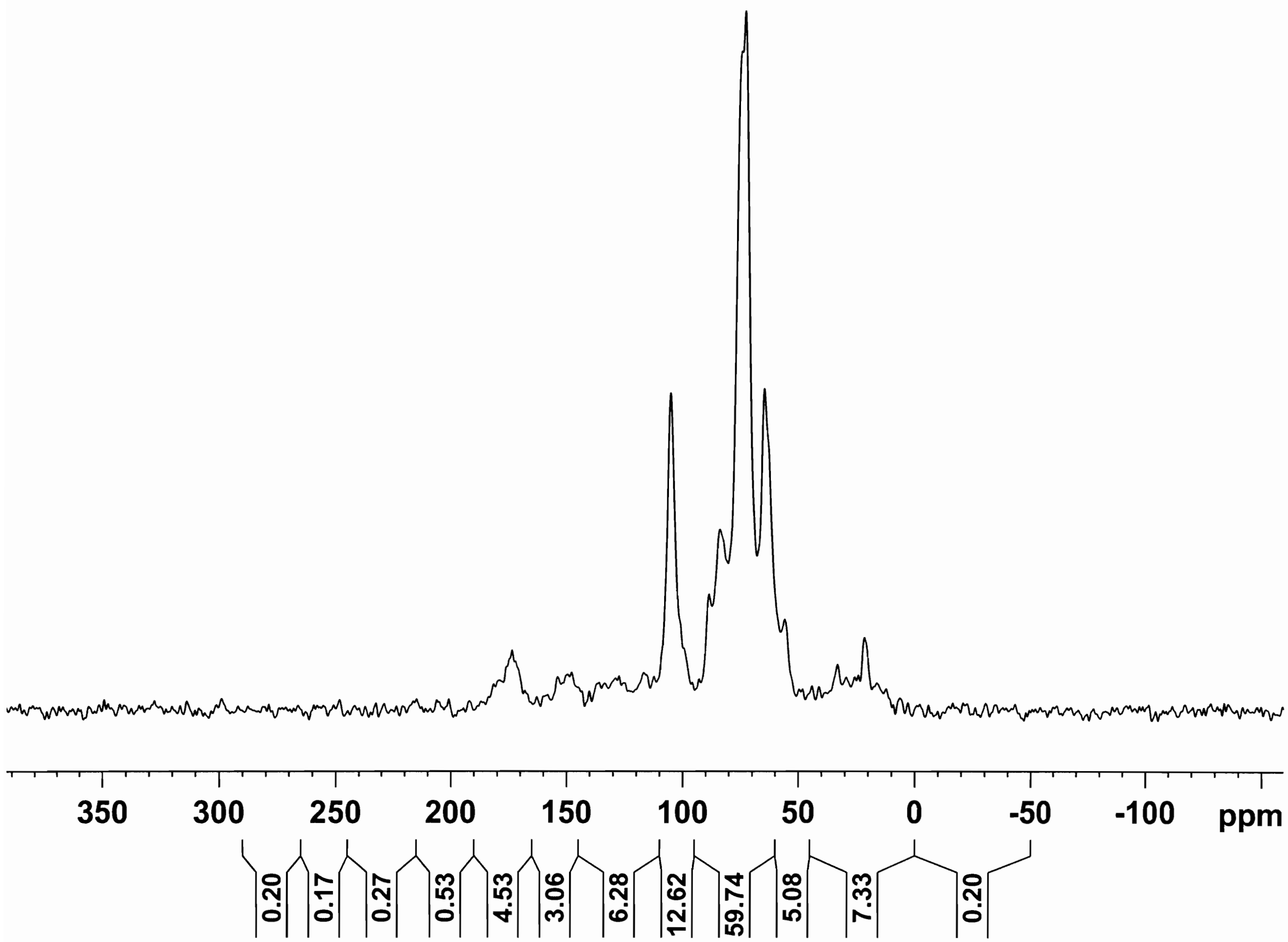
F2 - Acquisition Parameters
Date_             20080307
Time                 20.16
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                  1625.5
DW                  19.800 usec
DE                    6.00 usec
TE                   694.1 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.05 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229662 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 2, Cover Crop
11/28/2009   59.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

```
Current Data Parameters
NAME     KBSNRate_LS202_3A
EXPNO                    1
PROCNO                   1

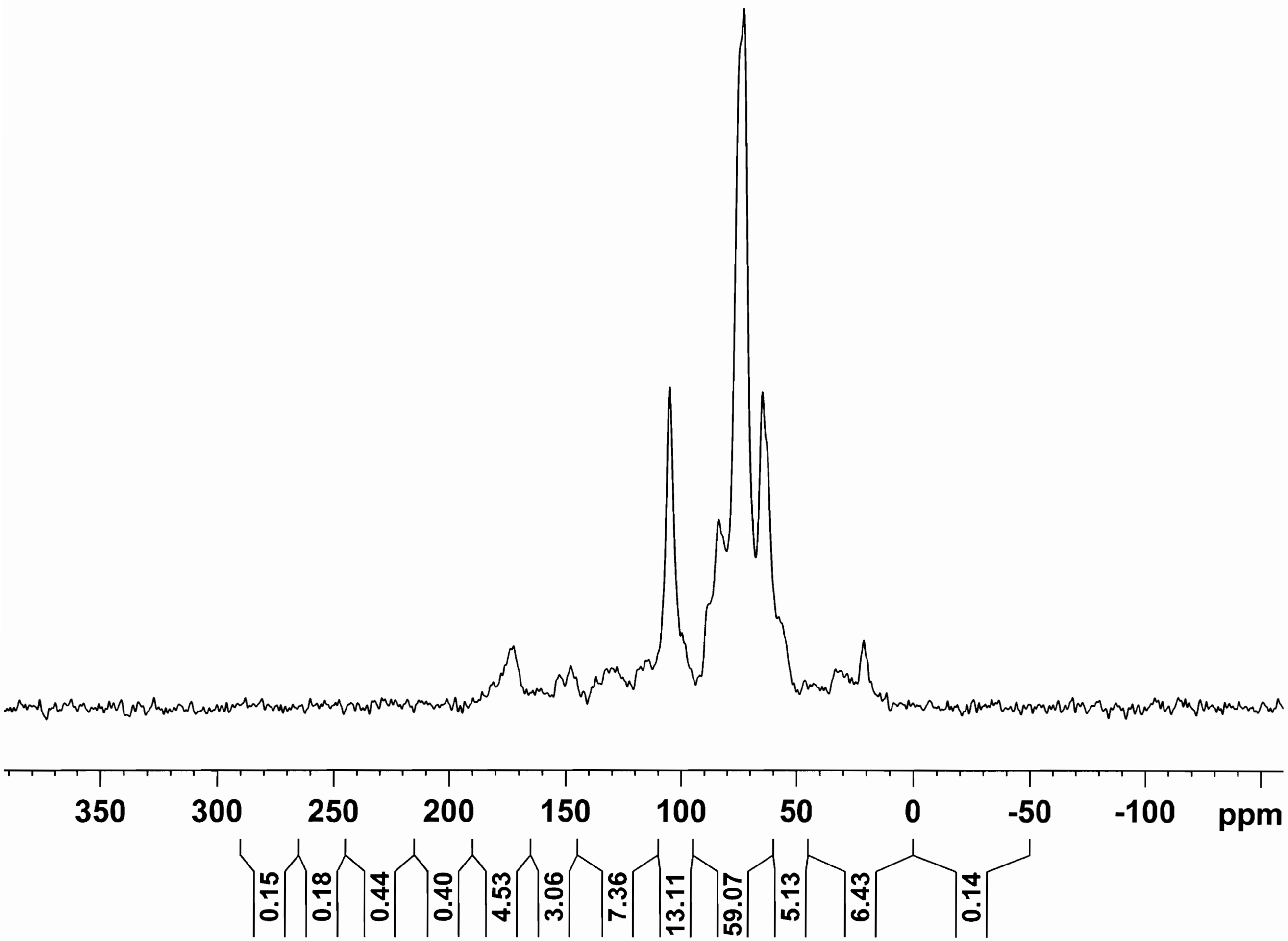
F2 - Acquisition Parameters
Date_             20091128
Time                 10.55
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                    2048
DW                 18.000 usec
DE                  17.00 usec
TE                  292.2 K
D1             3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15               1000.00 usec
PL1                  2.40 dB
SFO1           50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                    1H
P3                   3.15 usec
P31                  6.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 3, Cover Crop
11/27/2009 57.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

Current Data Parameters
NAME KBSNRate_LS305_3A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091127
Time 10.12
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.0 K
D1 3.00000000 sec
TD0 4

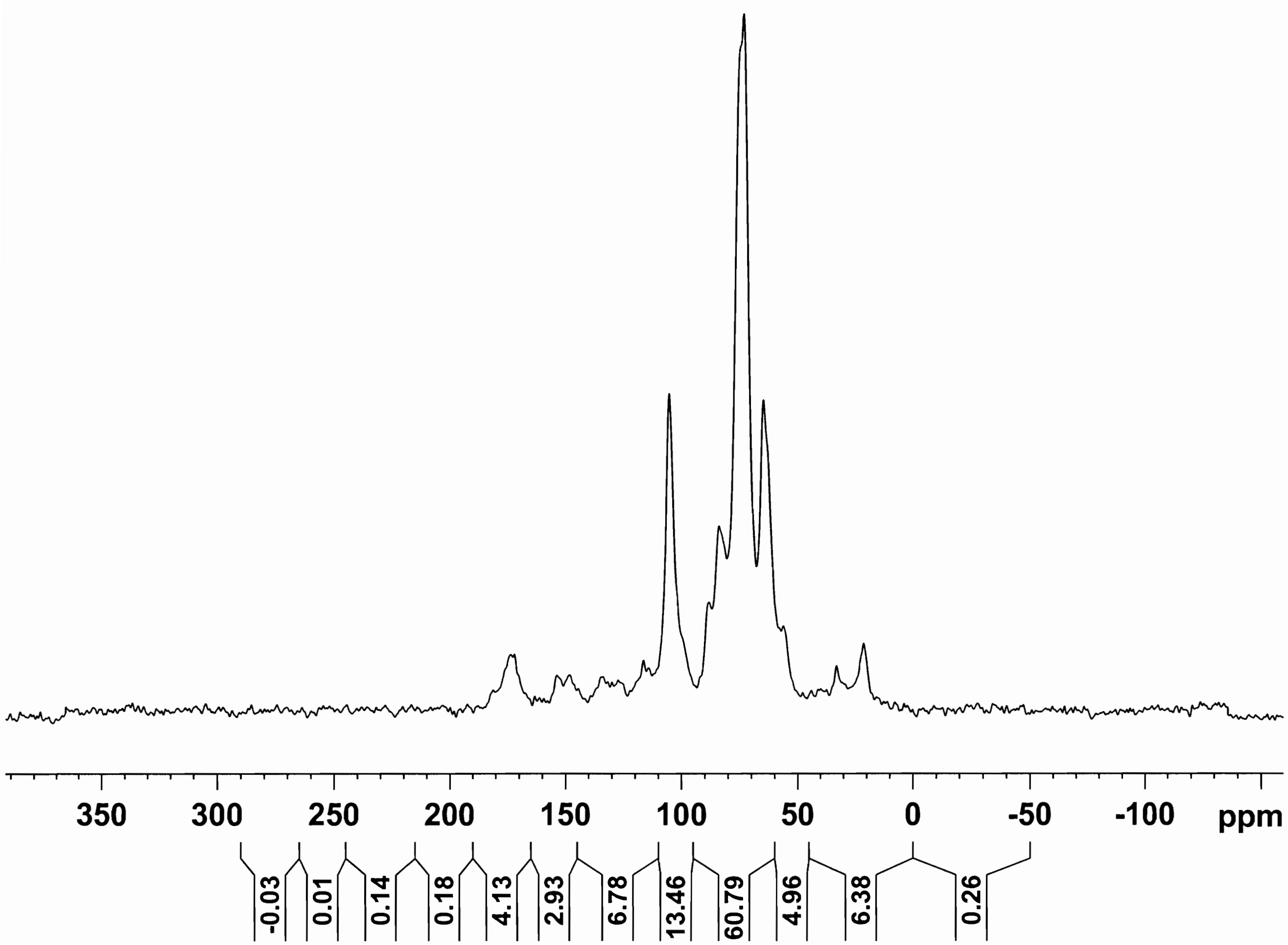
======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

336

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 4, Cover Crop
11/15/2009 59.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_LS404_3A
EXPNO                     1
PROCNO                    1

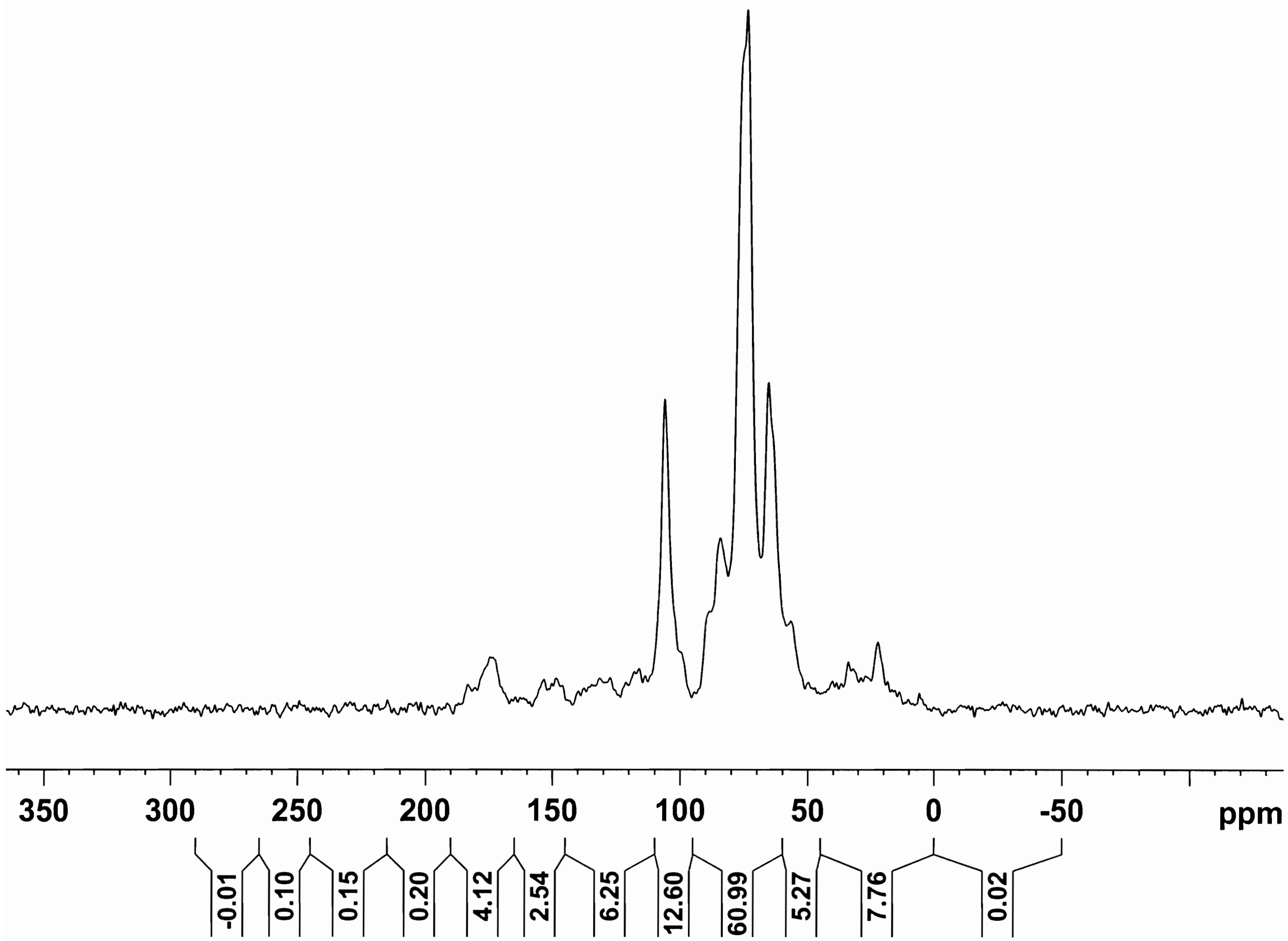
F2 - Acquisition Parameters
Date_              20091115
Time                  18.37
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                     1024
SOLVENT
NS                     2000
DS                        0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                     2048
DW                  18.000 usec
DE                   17.00 usec
TE                   292.4 K
D1              3.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                    13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.15 usec
P31                    6.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3228472 MHz
WDW                      EM
SSB                       0
LB                    40.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/08/2008   51.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_LS102_4A
EXPNO   1
PROCNO   1

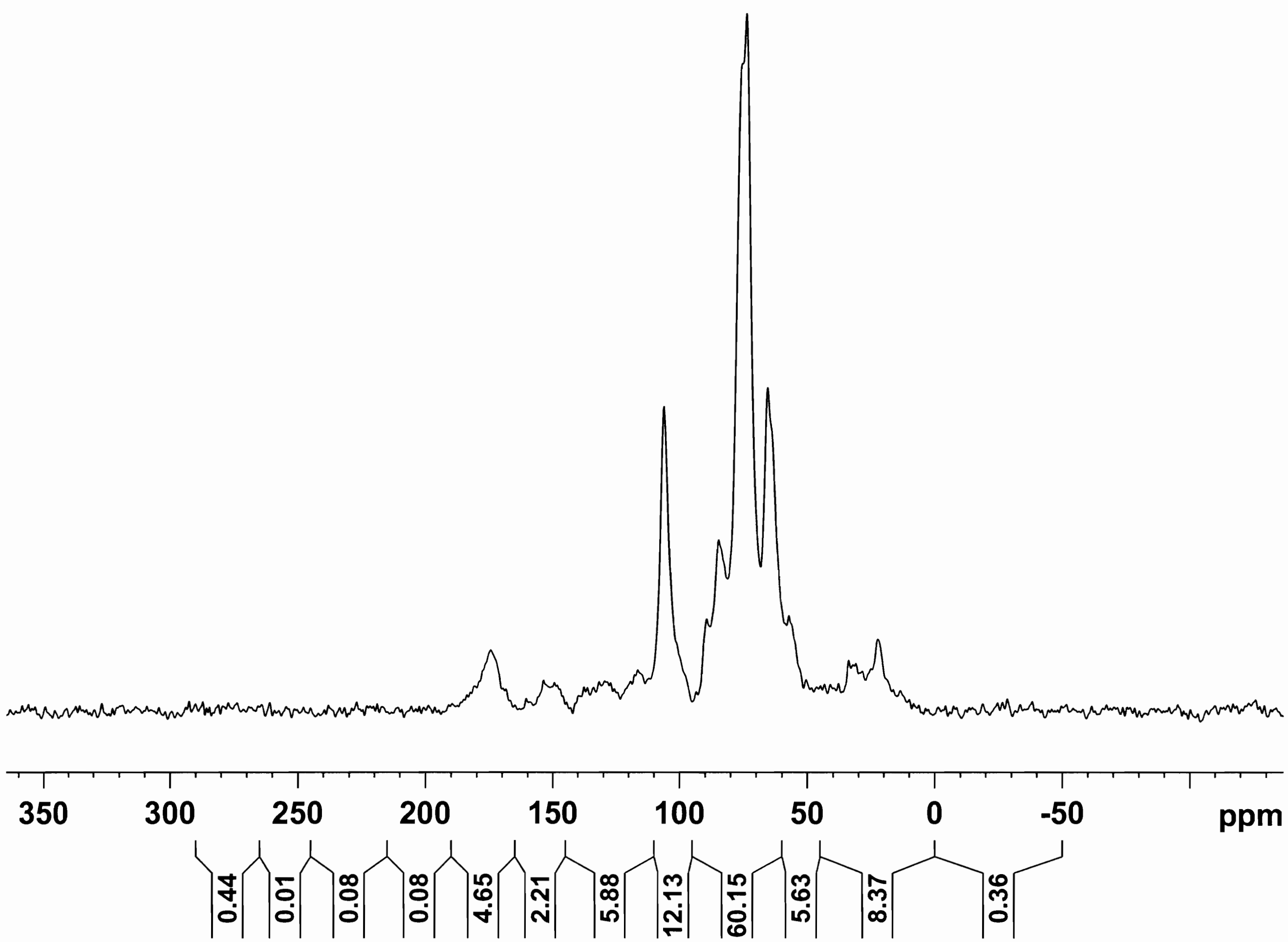
F2 - Acquisition Parameters
Date_   20080308
Time   11.43
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   2298.8
DW   19.800 usec
DE   6.00 usec
TE   694.0 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229662 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/09/2008   49.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_LS104_5A
EXPNO 1
PROCNO 1

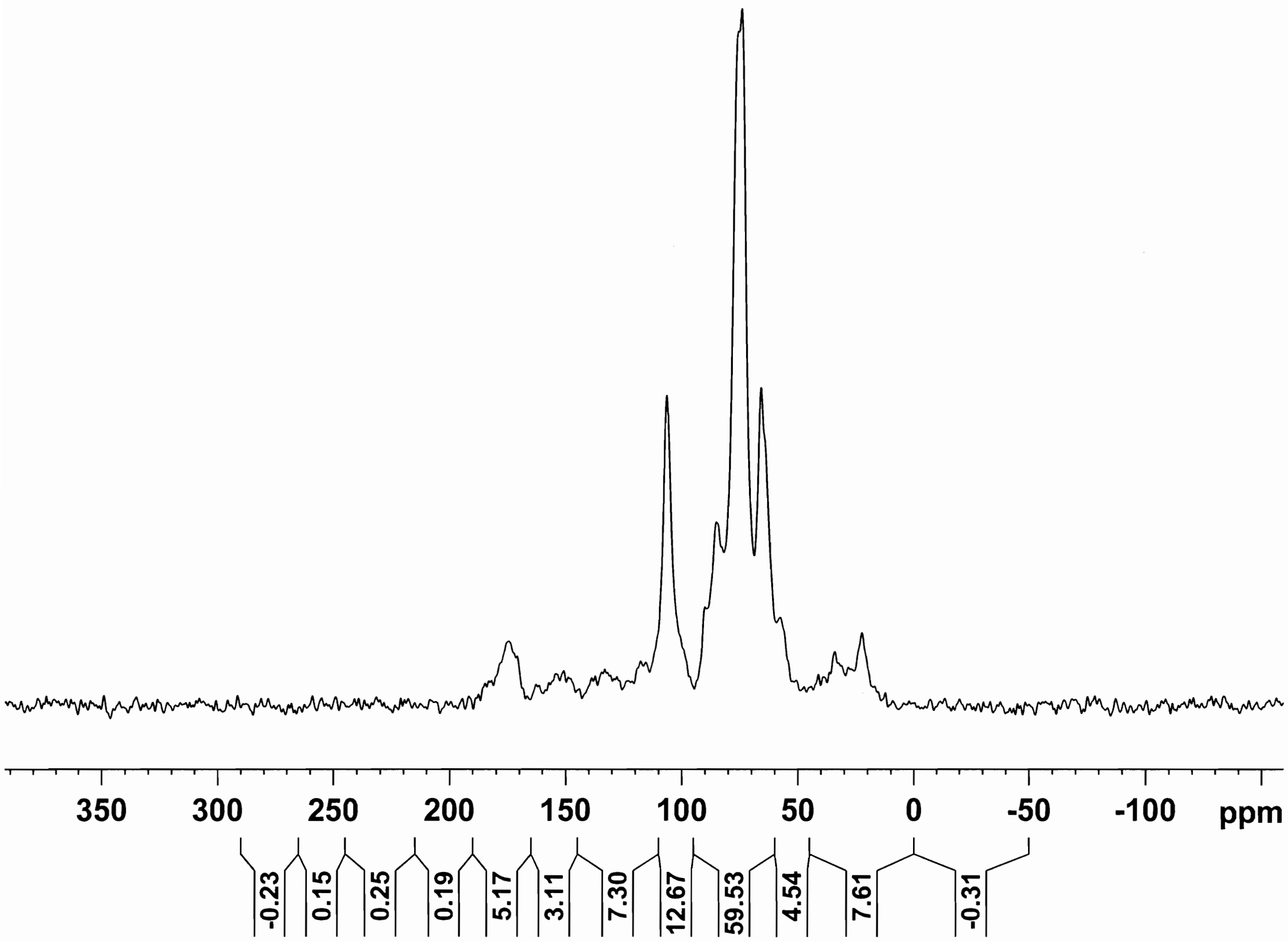
F2 - Acquisition Parameters
Date_ 20080309
Time 4.02
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 4597.6
DW 19.800 usec
DE 6.00 usec
TE 694.3 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 1.40 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229662 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 2, Cover Crop
01/04/2010   59.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_LS205_5A
EXPNO                    1
PROCNO                   1

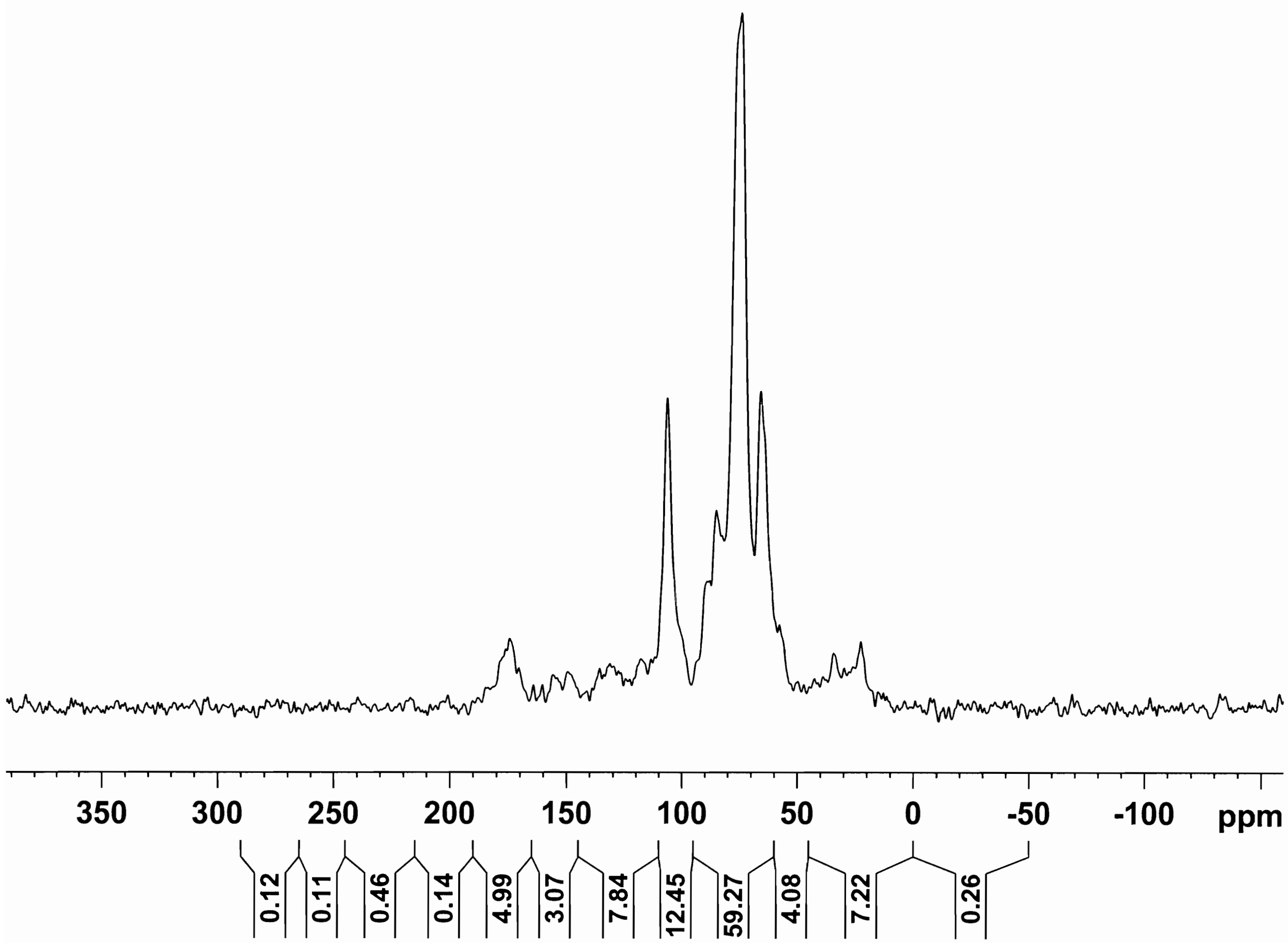
F2 - Acquisition Parameters
Date_             20100104
Time                 14.19
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   291.7 K
D1              3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 3, Cover Crop
01/04/2010   59.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_LS302_5A
EXPNO                    1
PROCNO                   1

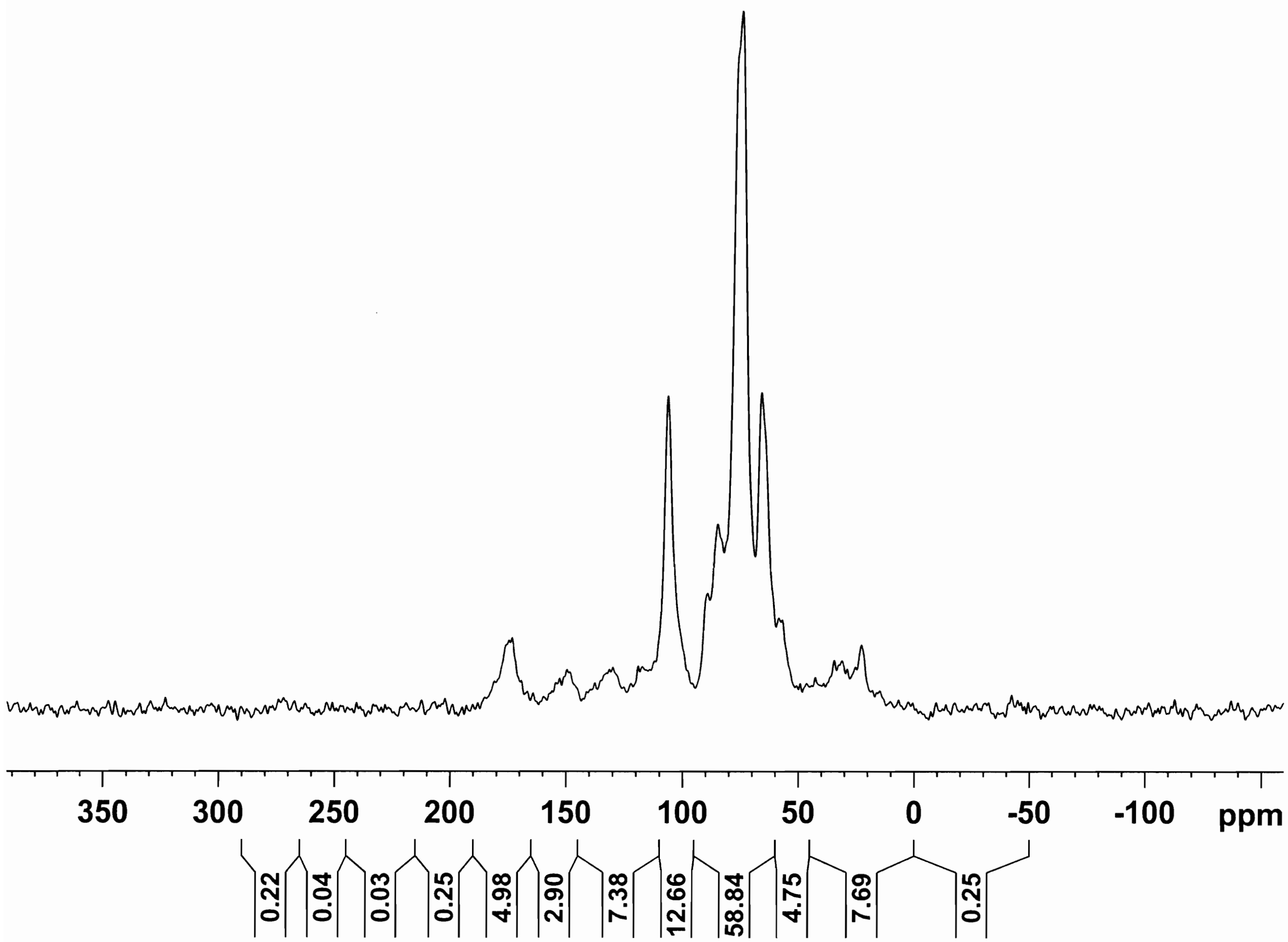
F2 - Acquisition Parameters
Date_             20100104
Time                 15.08
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   292.1 K
D1              3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 4, Cover Crop
01/04/2010   62.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME   KBSNRate_LS407_5A
EXPNO   1
PROCNO   1

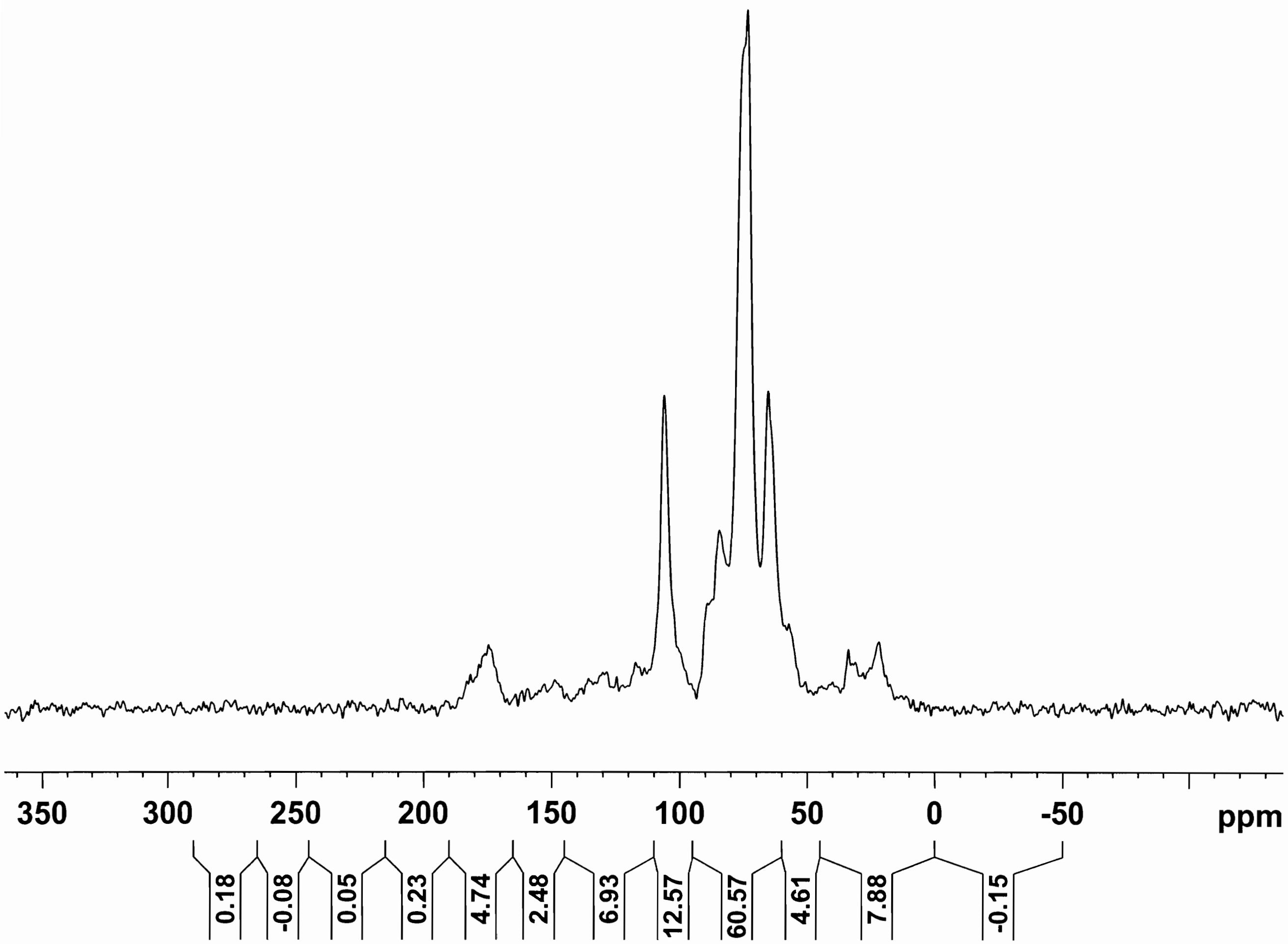
F2 - Acquisition Parameters
Date_   20100104
Time   16.17
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cp.99.WCH
TD   1024
SOLVENT
NS   1000
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   292.0 K
D1   3.00000000 sec
TD0   4

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.40 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.15 usec
P31   6.00 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

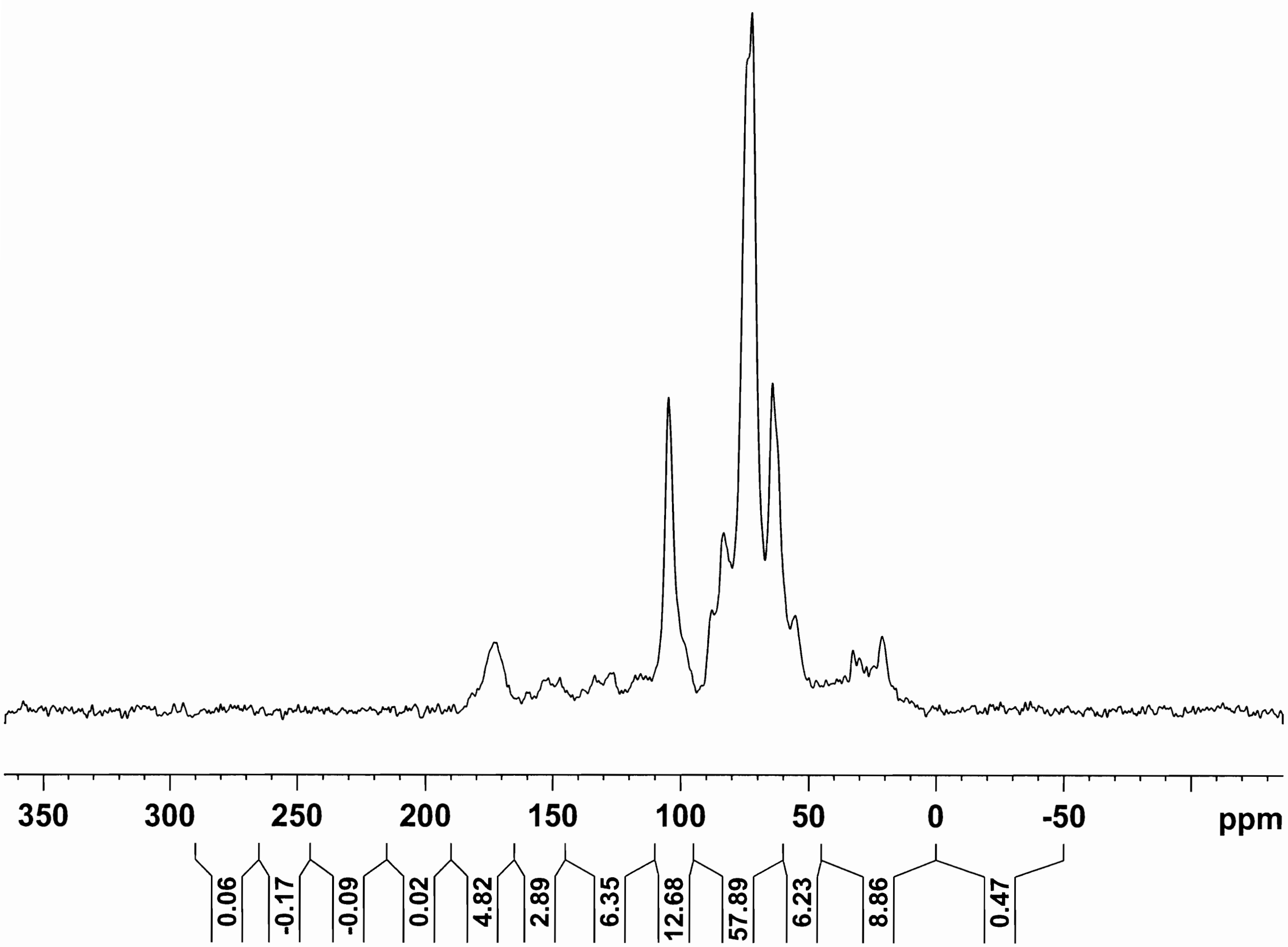
F2 - Processing parameters
SI   16384
SF   50.3228472 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/09/2008   48.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters	
NAME	KBSNRate_LS103_6A
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20080309
Time	19.11
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	4597.6
DW	19.800 usec
DE	6.00 usec
TE	694.6 K
D1	2.00000000 sec
======== CHANNEL f1 ========	
NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz
======== CHANNEL f2 ========	
CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz
F2 - Processing parameters	
SI	16384
SF	50.3229662 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/15/2008 52.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_LS105_7A
EXPNO 1
PROCNO 1

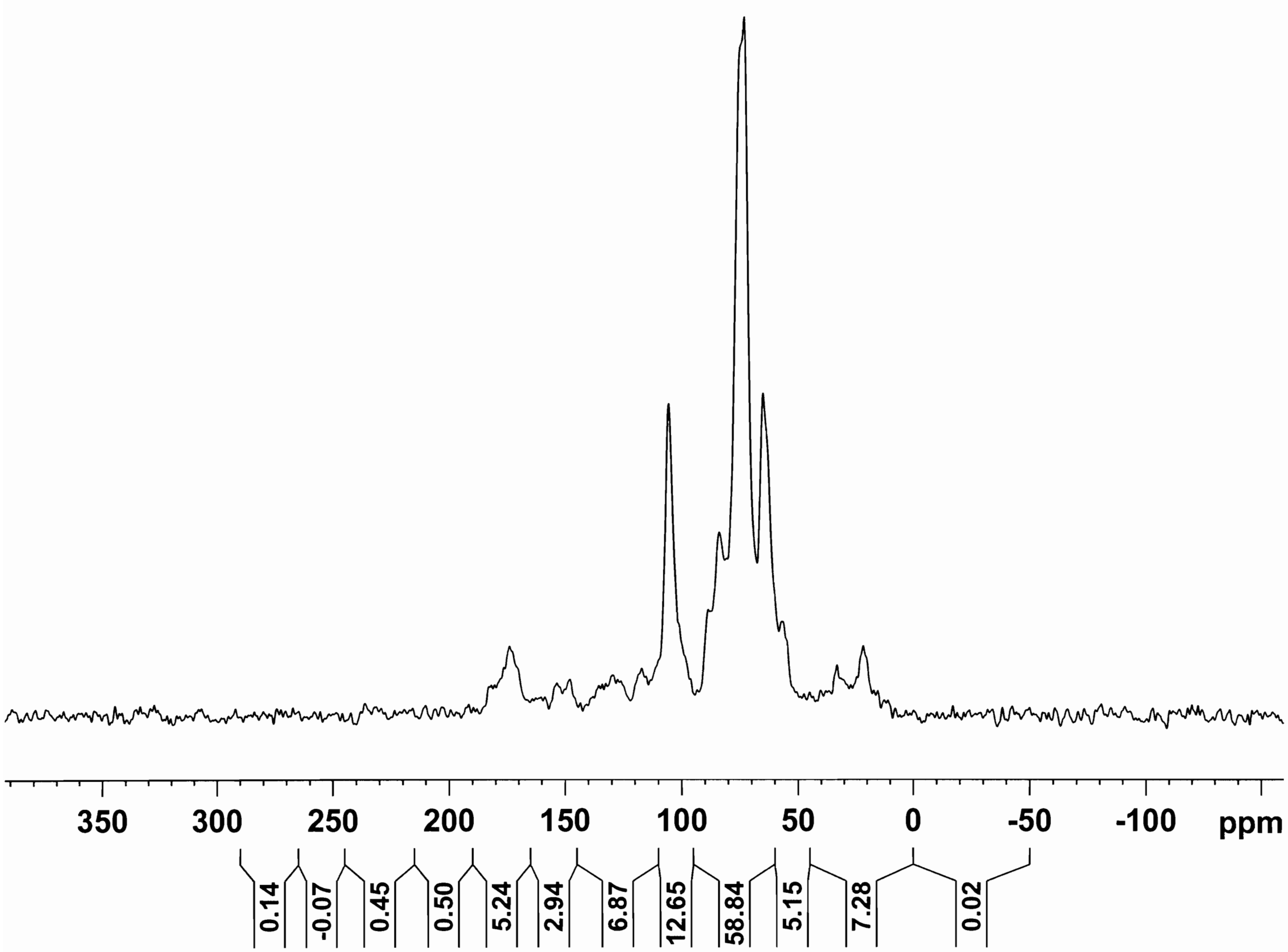
F2 - Acquisition Parameters
Date_ 20080215
Time 11.37
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 6502
DW 19.800 usec
DE 6.00 usec
TE 696.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 1.40 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229348 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 2, Cover Crop
12/28/2009   59.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_LS204_7A
EXPNO 1
PROCNO 1

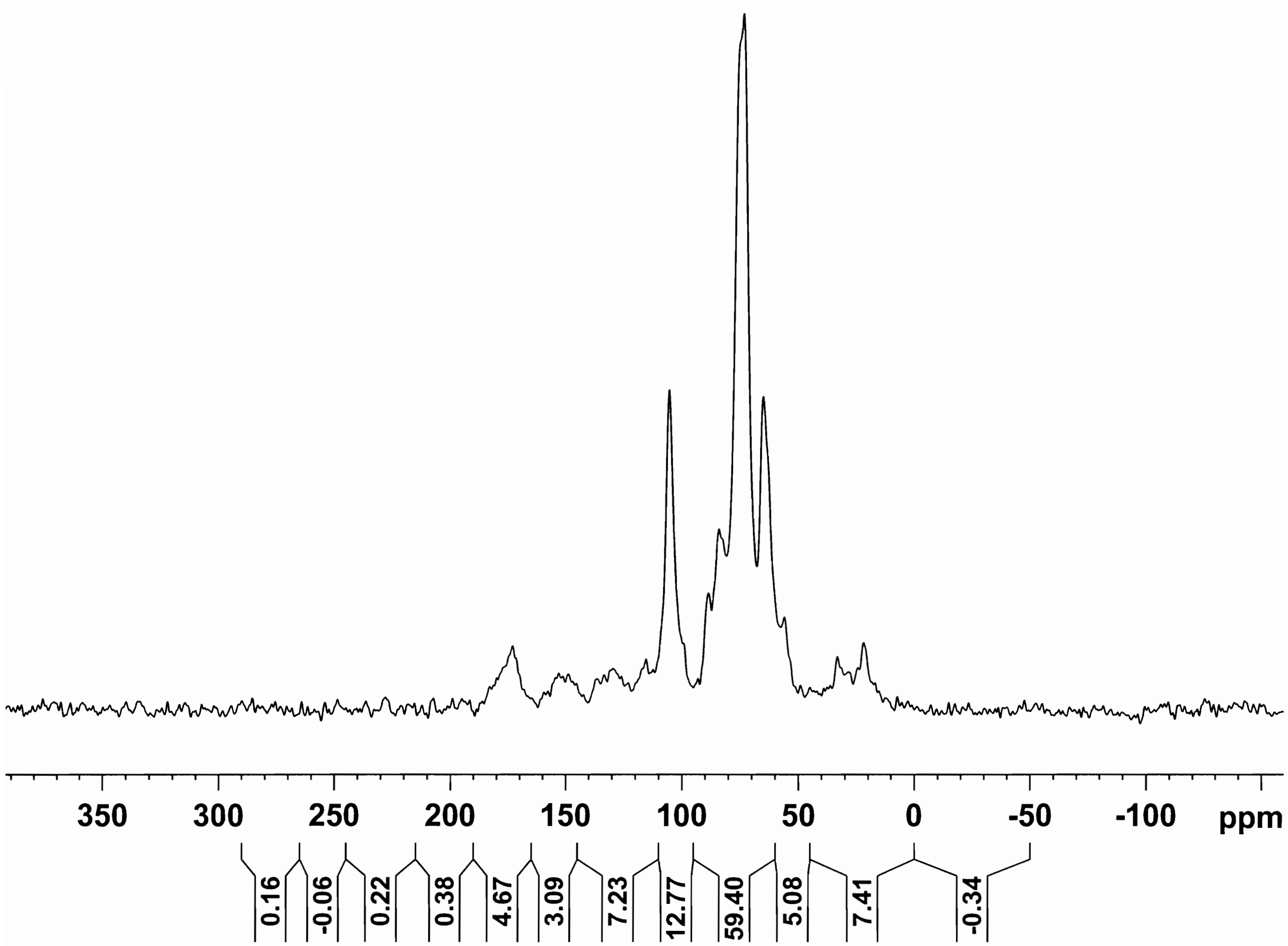
F2 - Acquisition Parameters
Date_ 20091228
Time 12.27
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.0 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 3, Cover Crop
12/28/2009   60.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_LS304_7A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091228
Time 13.26
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

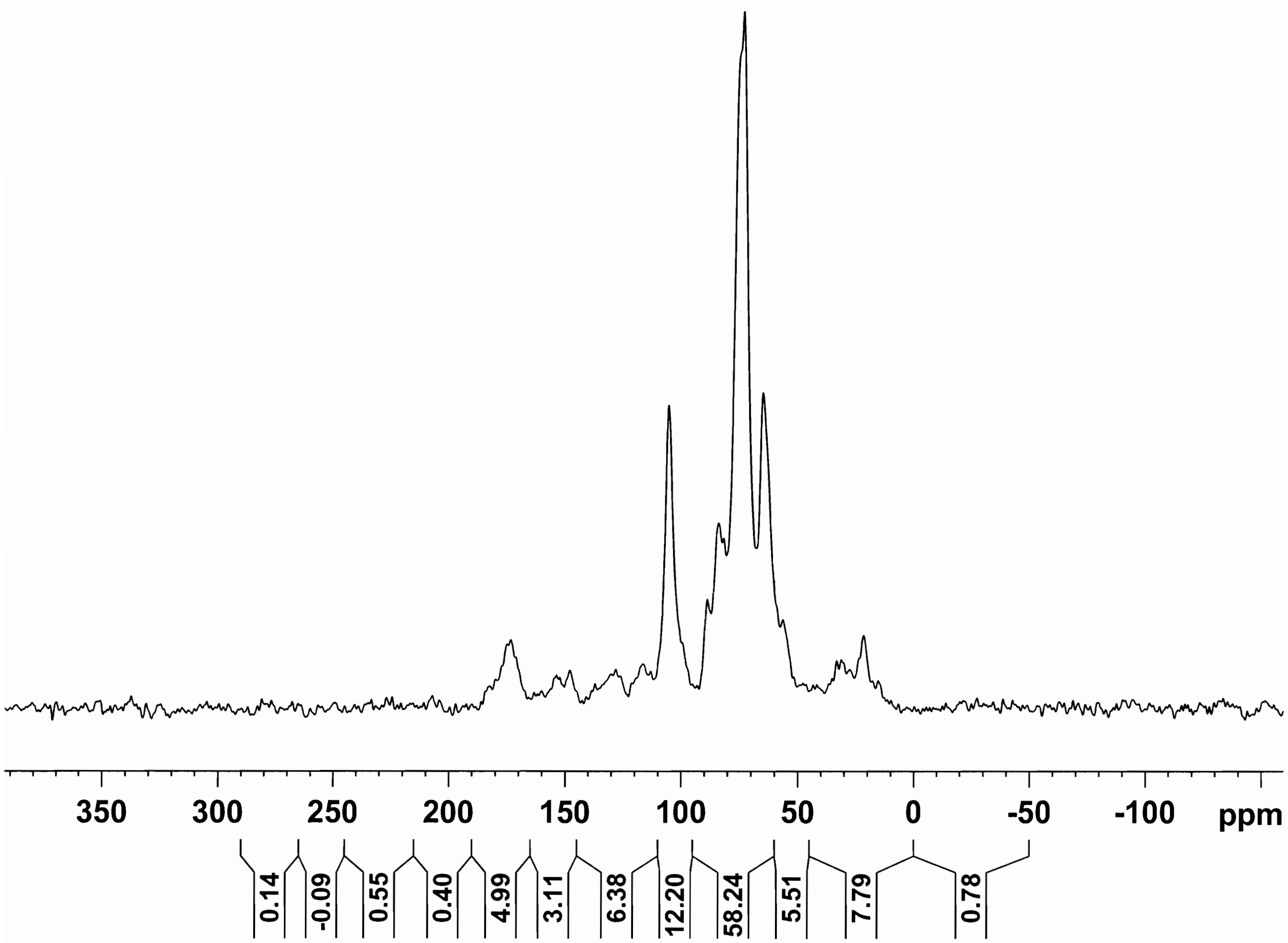
======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

346

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 4, Cover Crop
12/30/2009   61.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME       KBSNRate_LS406_7A
EXPNO                     1
PROCNO                    1

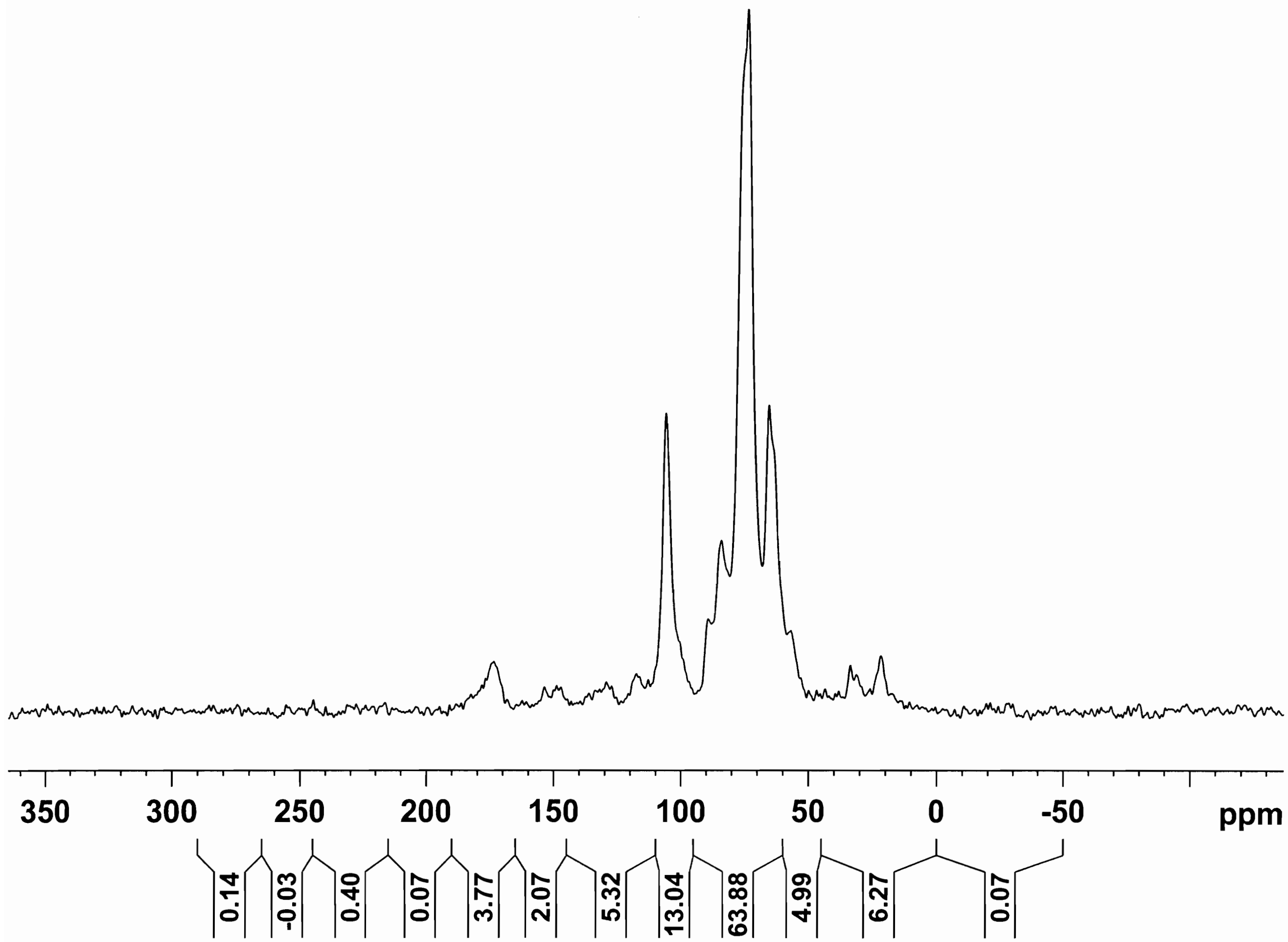
F2 - Acquisition Parameters
Date_            20091230
Time                14.31
INSTRUM             spect
PROBHD    4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                   1024
SOLVENT
NS                   1000
DS                      0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                   2048
DW                 18.000 usec
DE                  17.00 usec
TE                  292.0 K
D1             3.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  2.40 dB
SFO1           50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.15 usec
P31                  6.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3228472 MHz
WDW                    EM
SSB                     0
LB                  40.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/15/2008   52.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_LS101_1B
EXPNO   1
PROCNO   1

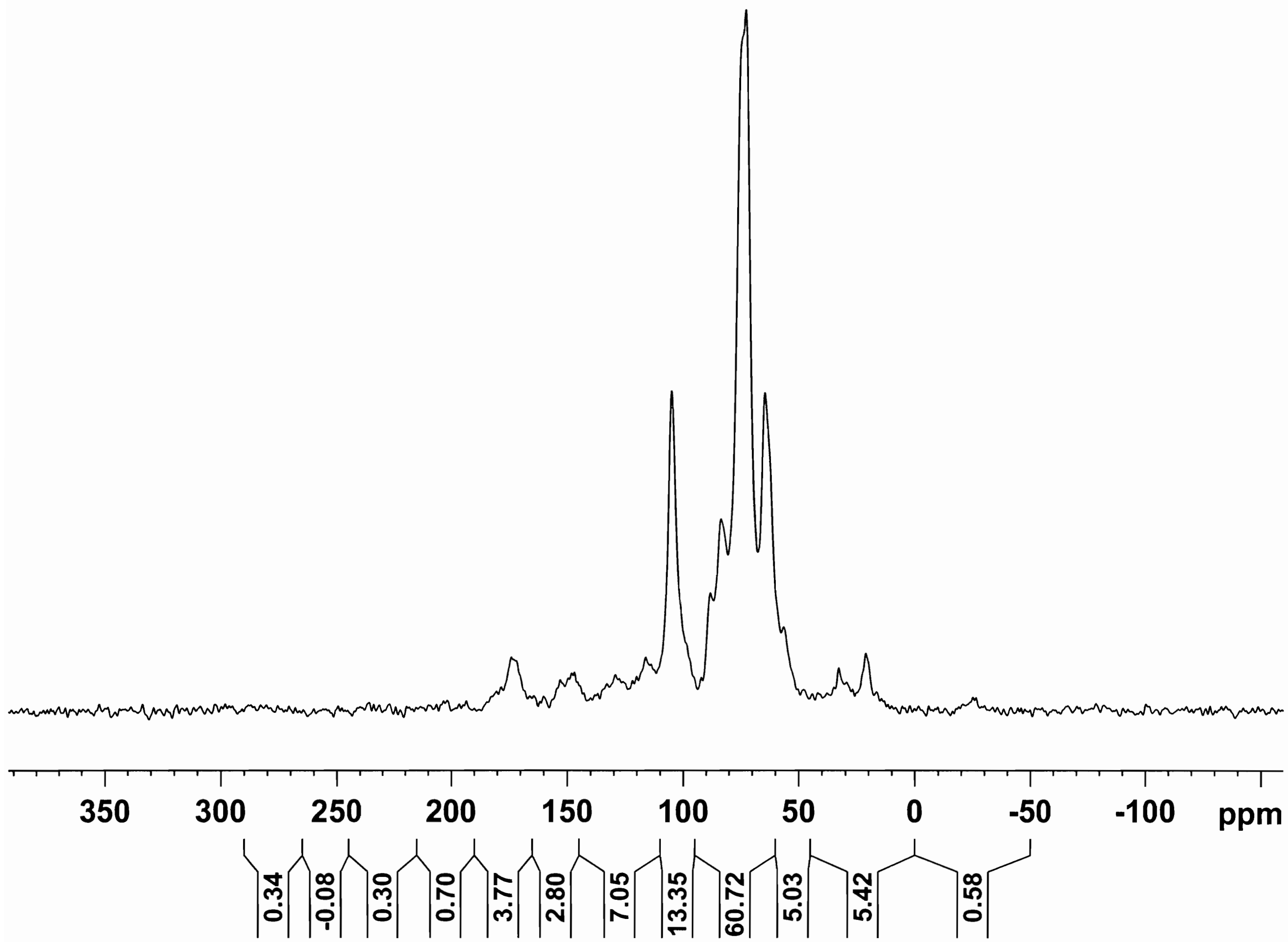
F2 - Acquisition Parameters
Date_   20080315
Time   4.05
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   574.7
DW   19.800 usec
DE   6.00 usec
TE   696.1 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229662 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 2, No Cover Crop
11/11/2009   58.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_LS203-1B
EXPNO 1
PROCNO 1

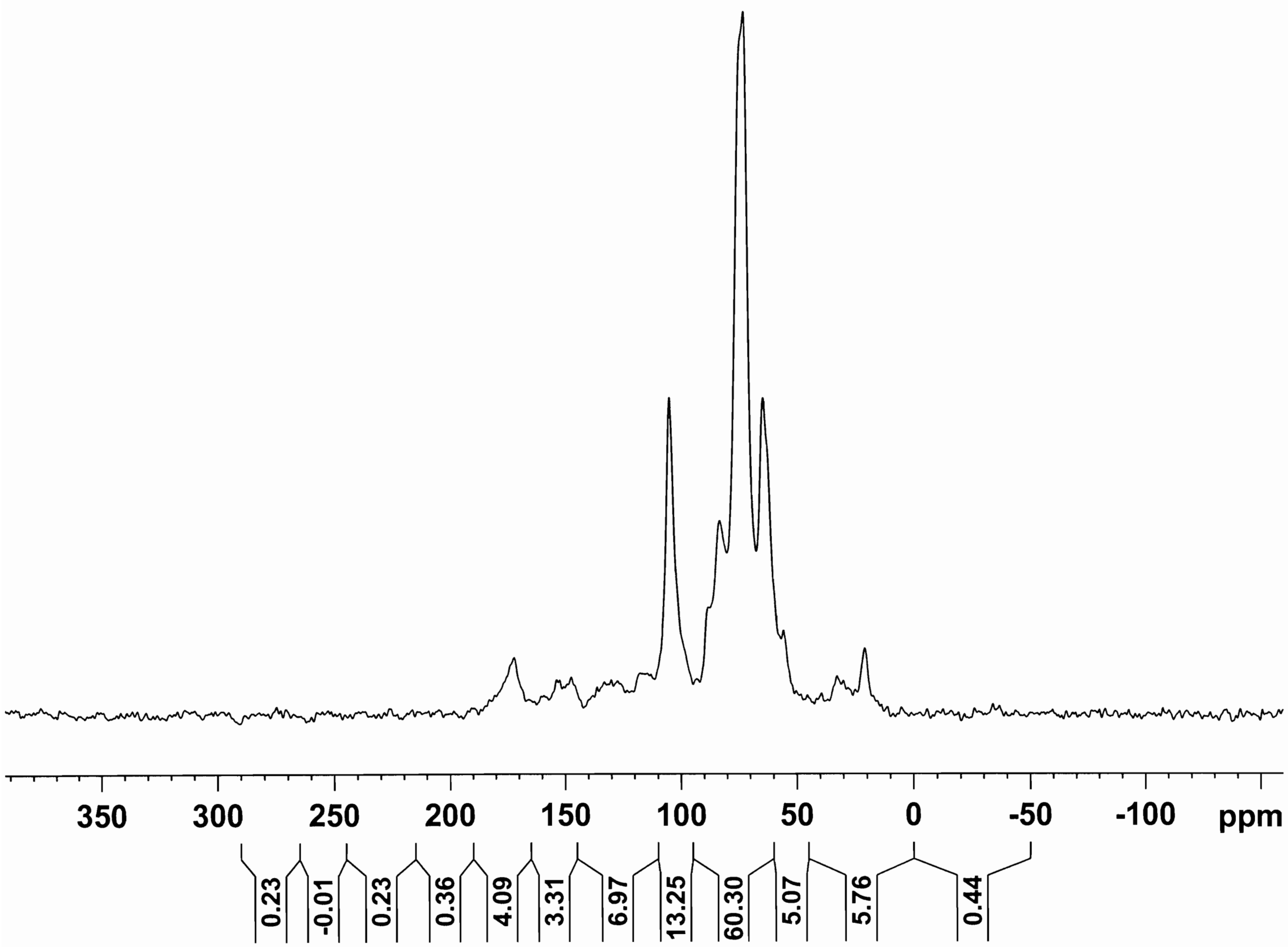
F2 - Acquisition Parameters
Date_ 20091111
Time 18.24
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 2000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 8

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 3, No Cover Crop
11/12/2009   63.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_LS307_1B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091112	
Time	15.05	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1989	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	292.8	K
D1	3.00000000	sec
TD0	8	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 4, No Cover Crop
11/12/2009 61.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.

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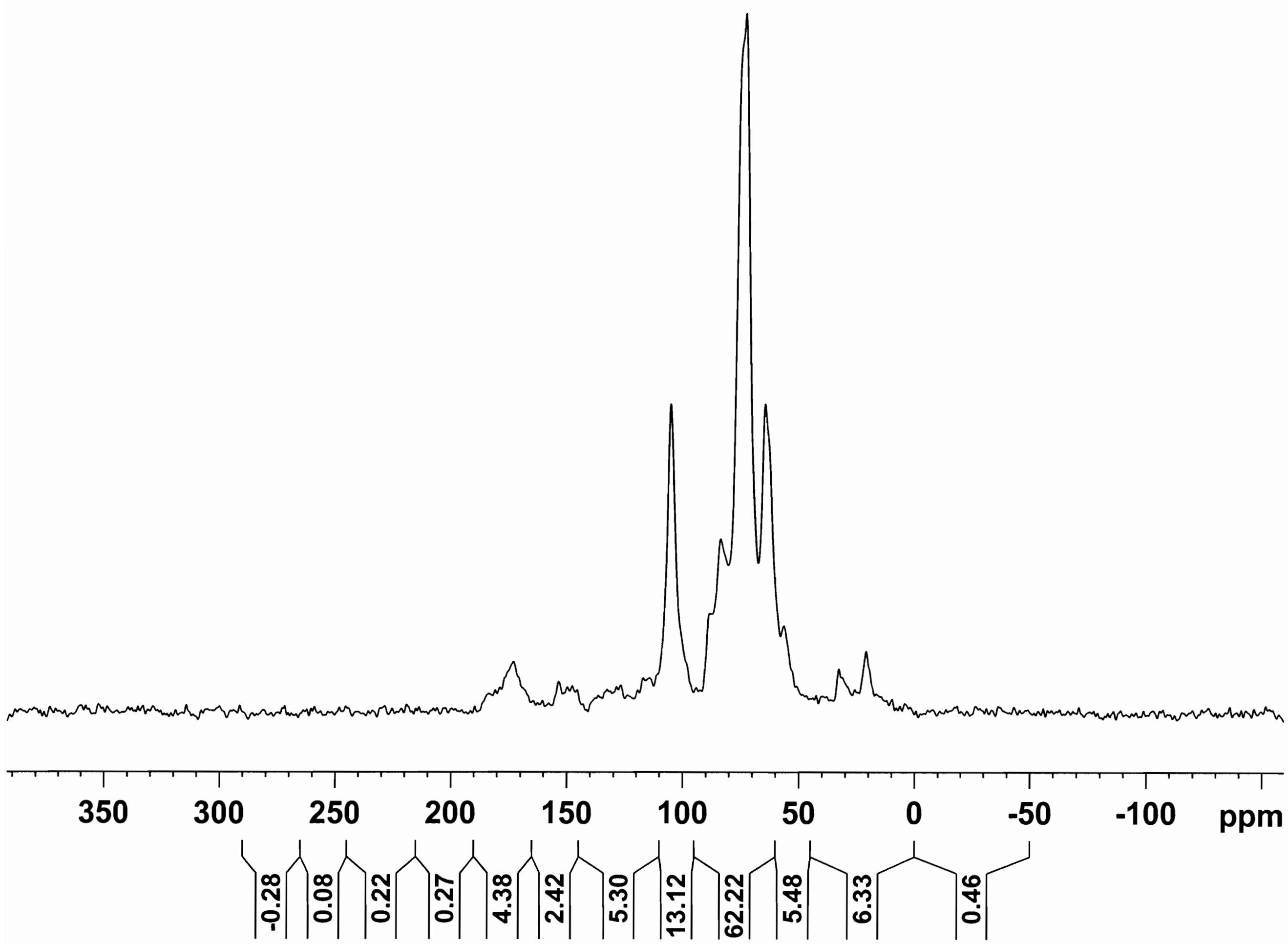
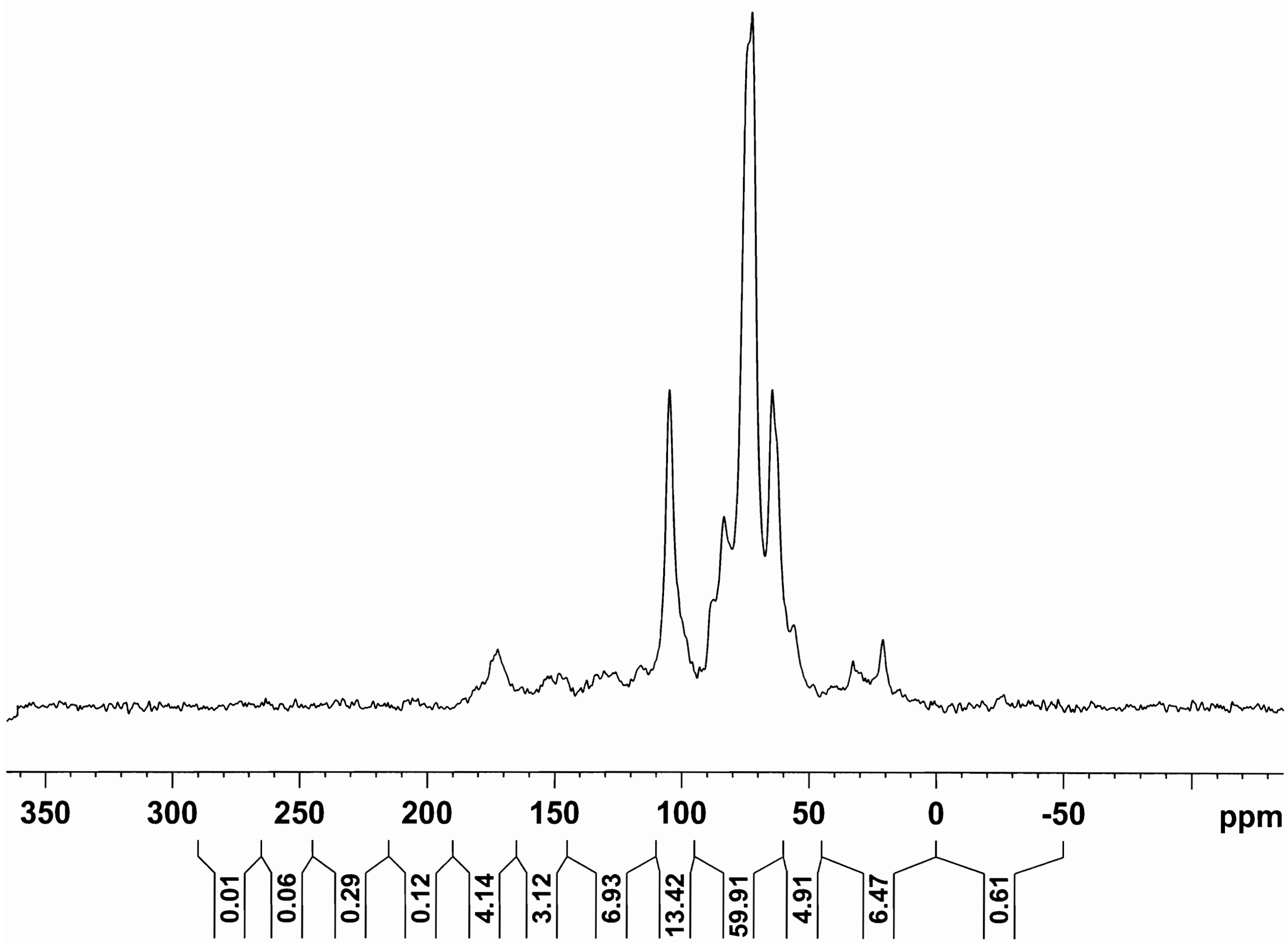


Current Data Parameters	
NAME	KBSNRate_LS402_1B
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20091112
Time	19.22
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.5 K
D1	3.00000000 sec
TD0	8
======== CHANNEL f1 ========	
NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz
======== CHANNEL f2 ========	
CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz
F2 - Processing parameters	
SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
06/28/2008 63.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME        KBSNRate_LS107_2B
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20080628
Time                   19.27
INSTRUM                spect
PROBHD      4 mm MASxvt BB
PULPROG           cp.99.LBA
TD                      1024
SOLVENT
NS                      3500
DS                         0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                      2048
DW                    19.800 usec
DE                      6.00 usec
TE                     697.1 K
D1                2.00000000 sec

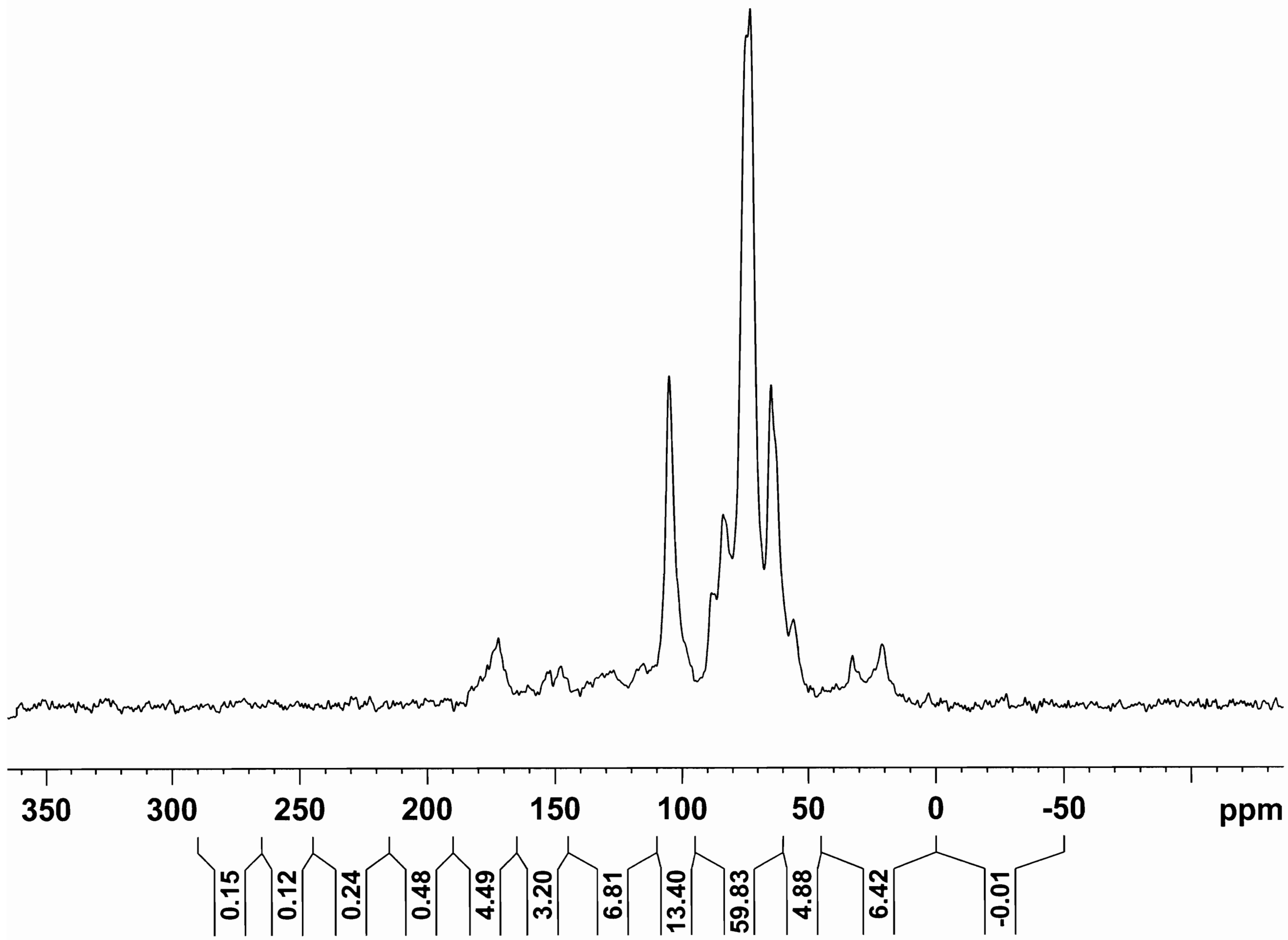
======== CHANNEL f1 ========
NUC1                     13C
P15                  1000.00 usec
PL1                     1.40 dB
SFO1              50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                      3.20 usec
P31                     5.10 usec
PL2                     6.00 dB
PL12                    3.00 dB
SFO2             200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF                50.3229333 MHz
WDW                       EM
SSB                        0
LB                     30.00 Hz
GB                         0
PC                      1.00
```

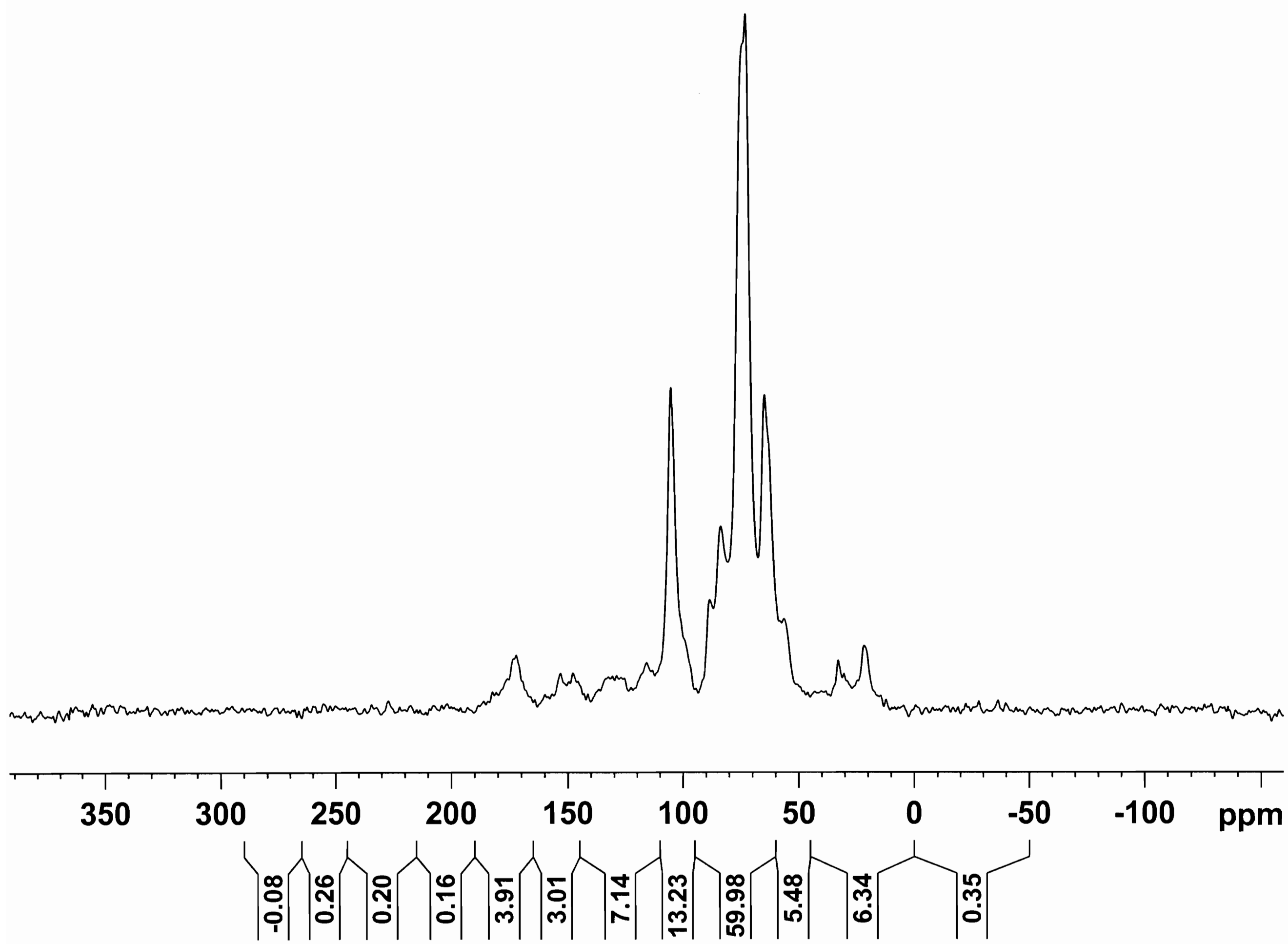
352

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/24/2008 55.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters	
NAME	KBSNRate_LS106_3B
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20080624
Time	21.03
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2048
DW	19.800 usec
DE	6.00 usec
TE	697.8 K
D1	2.00000000 sec
======== CHANNEL f1 ========	
NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz
======== CHANNEL f2 ========	
CPDPRG2	tppm15
NUC2	1H
P3	3.20 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz
F2 - Processing parameters	
SI	16384
SF	50.3229333 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 2, No Cover Crop
11/14/2009   58.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_LS202_3B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091114
Time	16.34
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.4 K
D1	3.00000000 sec
TD0	8

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

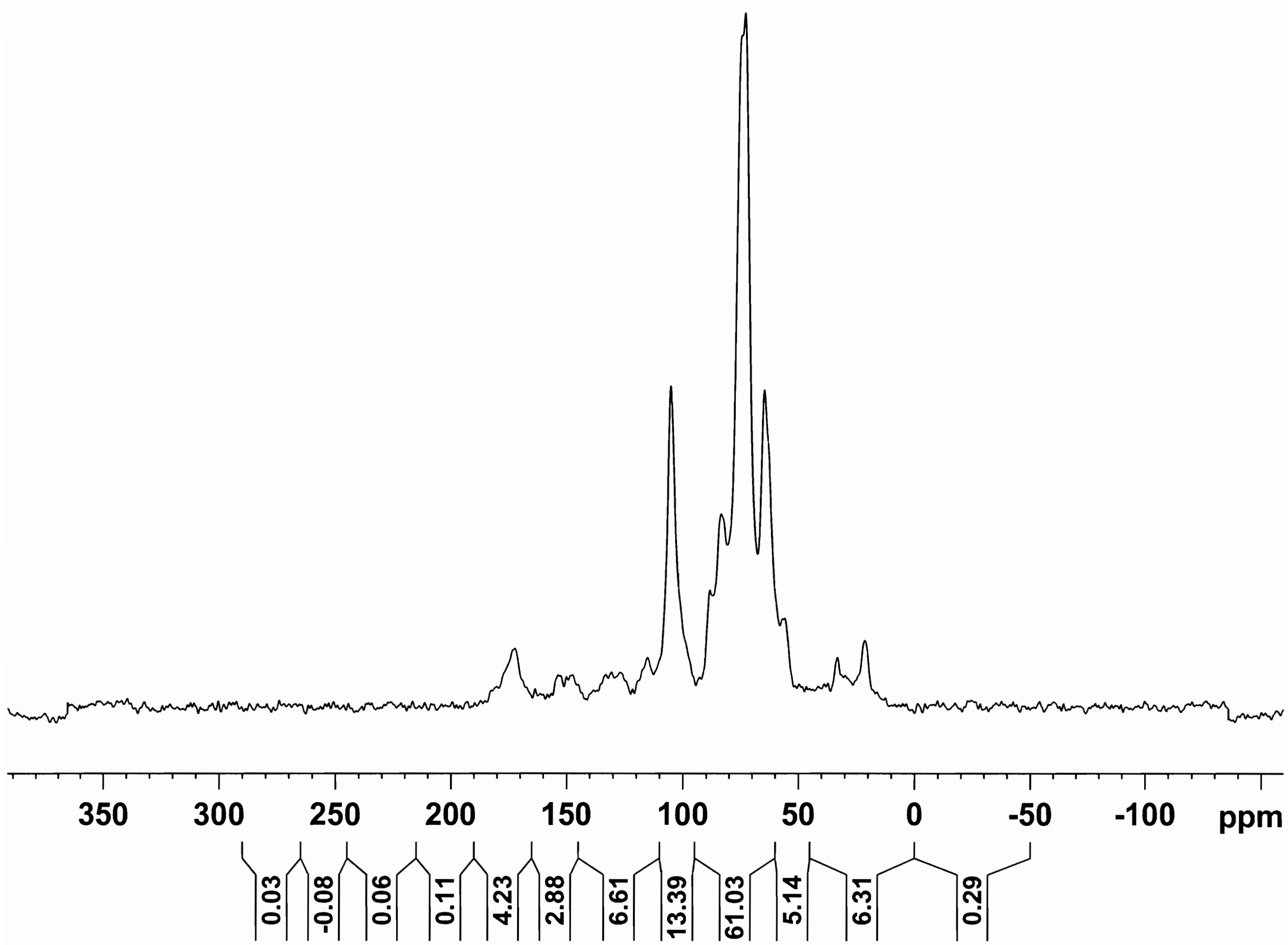
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 3, No Cover Crop
11/14/2009   62.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_LS305_3B
EXPNO   1
PROCNO   1

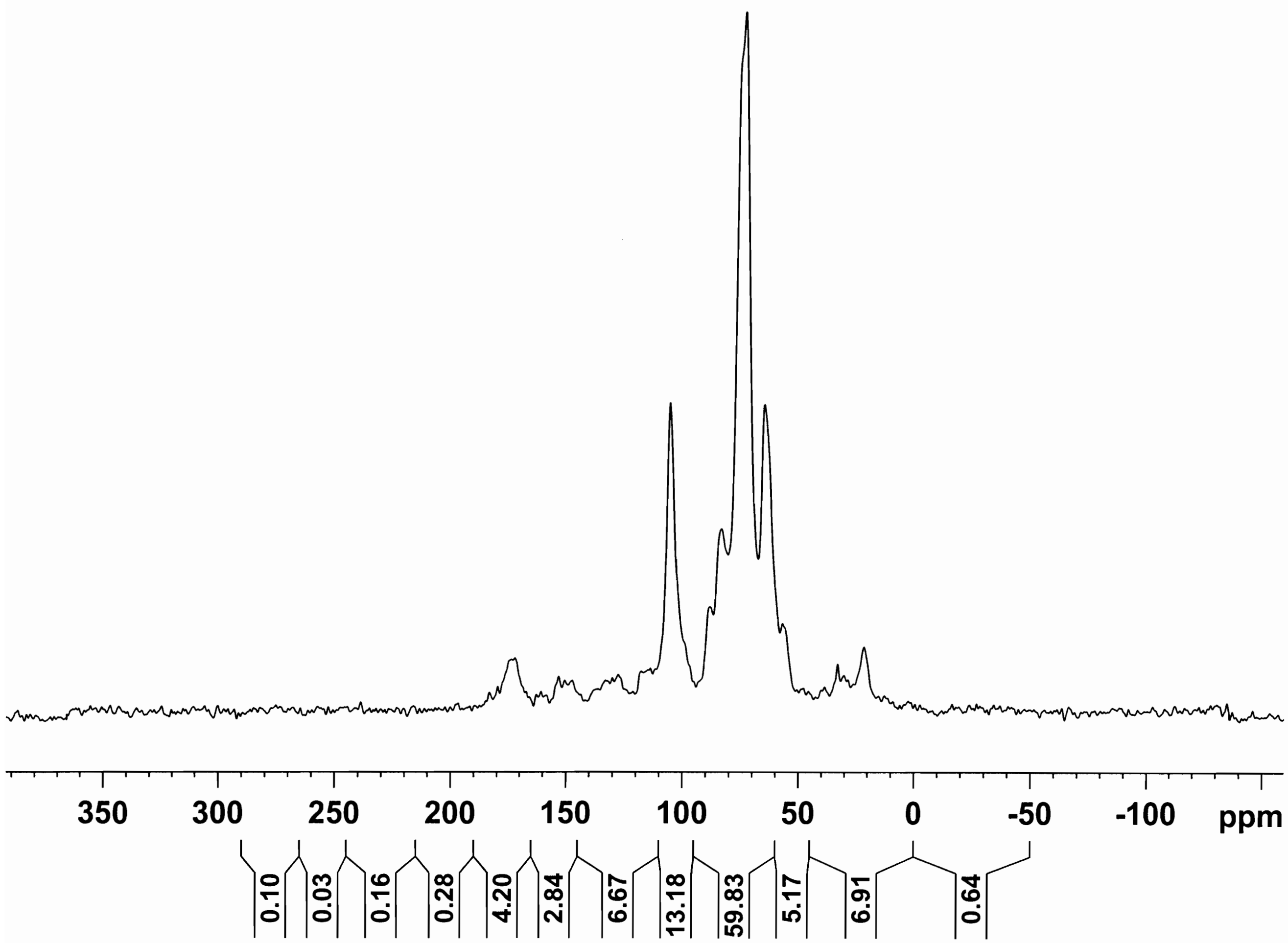
F2 - Acquisition Parameters
Date_   20091114
Time   18.10
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.WCH
TD   1024
SOLVENT
NS   2000
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   292.4 K
D1   3.00000000 sec
TD0   8

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.40 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.15 usec
P31   6.00 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228472 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 4, No Cover Crop
11/15/2009 59.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters

NAME	KBSNRate_LS404_3B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091115
Time	9.39
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.4 K
D1	3.00000000 sec
TD0	8

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

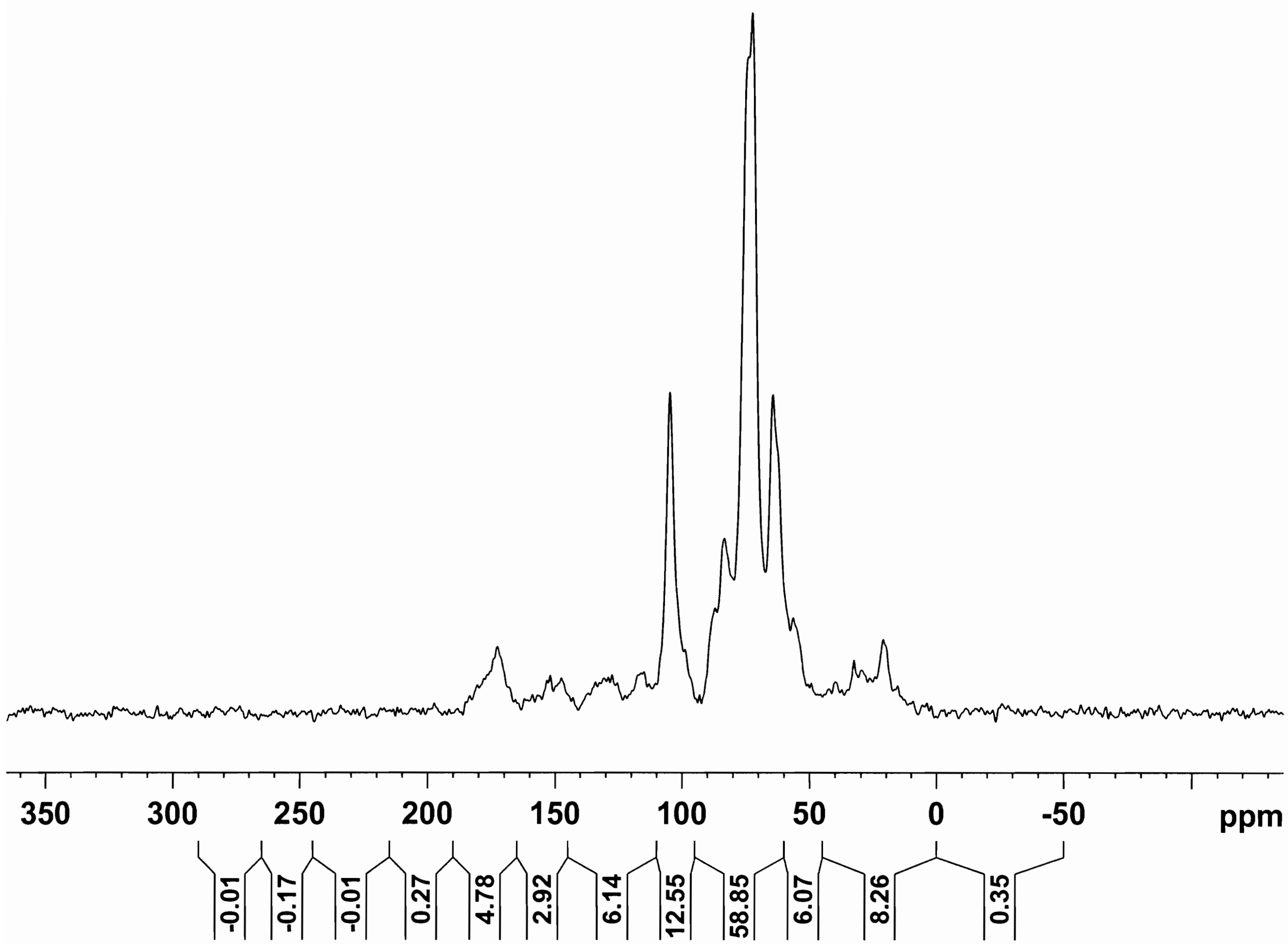
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/25/2008   52.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_LS102_4B
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080625
Time                 19.04
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                    2048
DW                  19.800 usec
DE                    6.00 usec
TE                   696.0 K
D1              2.00000000 sec

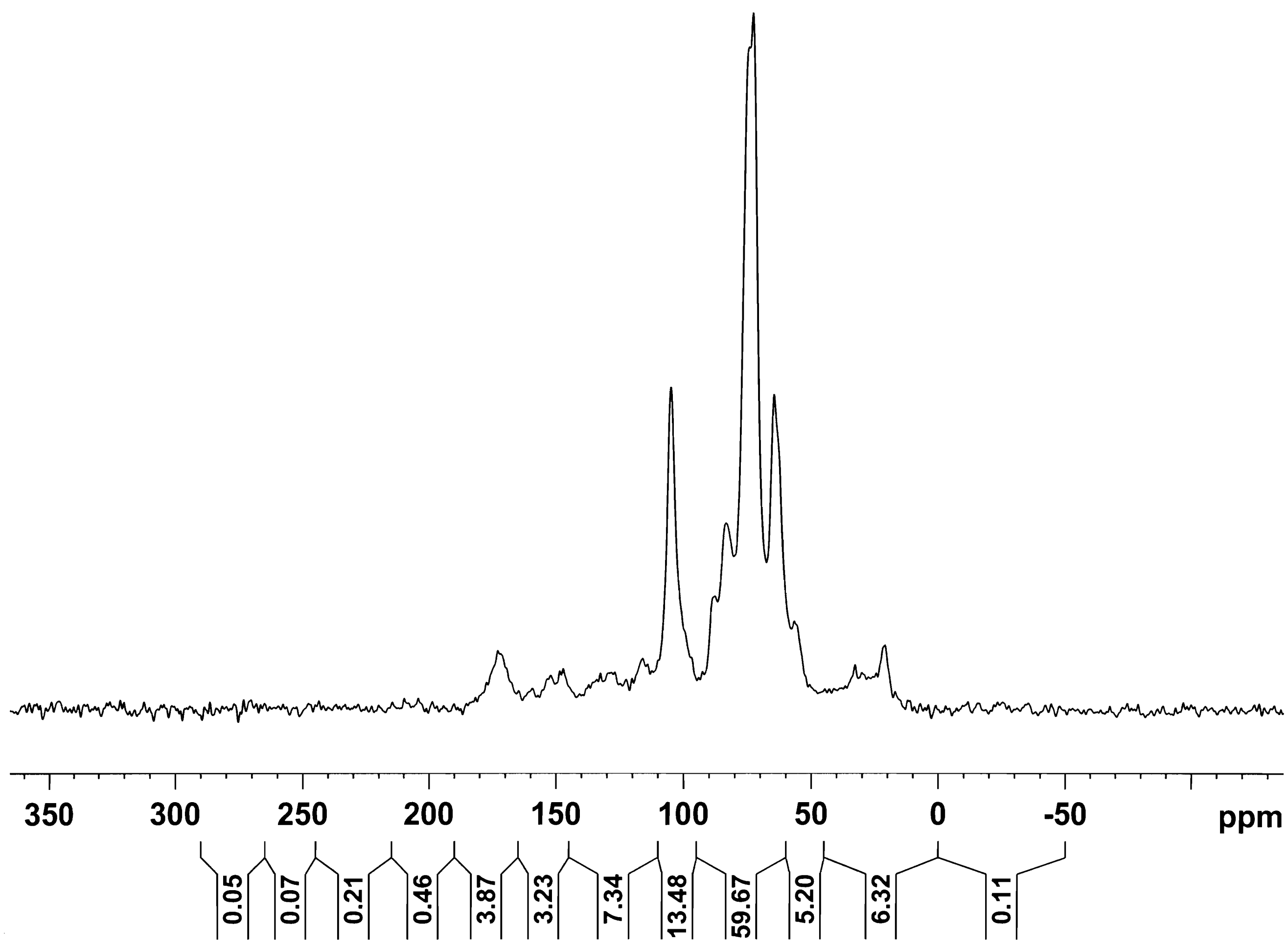
======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.20 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229333 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

357

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/26/2008   51.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME       KBSNRate_LS104_5B
EXPNO                      1
PROCNO                     1

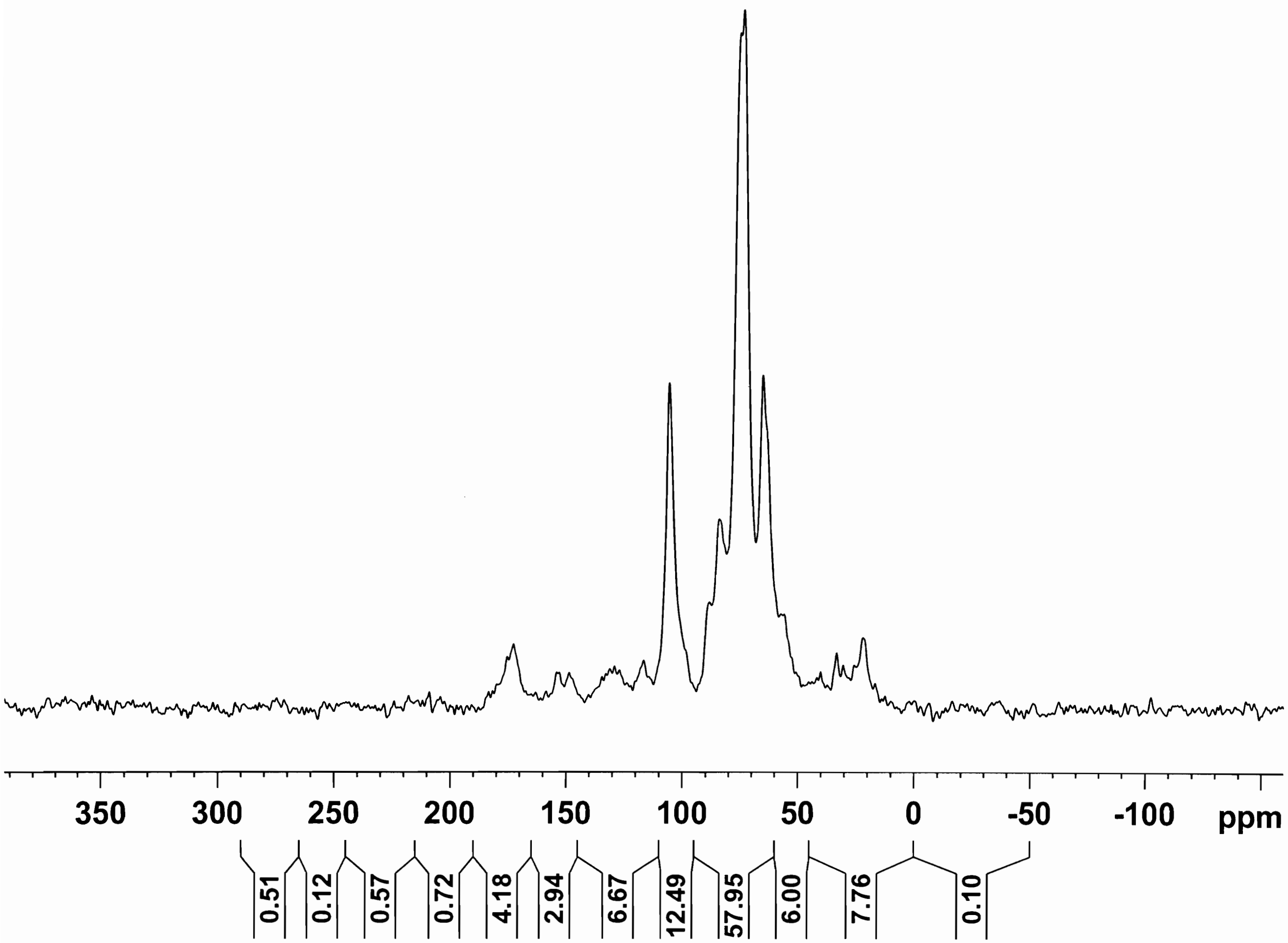
F2 - Acquisition Parameters
Date_               20080626
Time                   17.14
INSTRUM                spect
PROBHD      4 mm MASxvt BB
PULPROG            cp.99.LBA
TD                      1024
SOLVENT
NS                      3500
DS                         0
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                      2048
DW                19.800 usec
DE                  6.00 usec
TE                 696.0 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P15              1000.00 usec
PL1                  1.40 dB
SFO1          50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                  3.20 usec
P31                 5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF            50.3229333 MHz
WDW                       EM
SSB                        0
LB                  30.00 Hz
GB                         0
PC                      1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 2, No Cover Crop
12/30/2009   60.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_LS205_5B
EXPNO 1
PROCNO 1

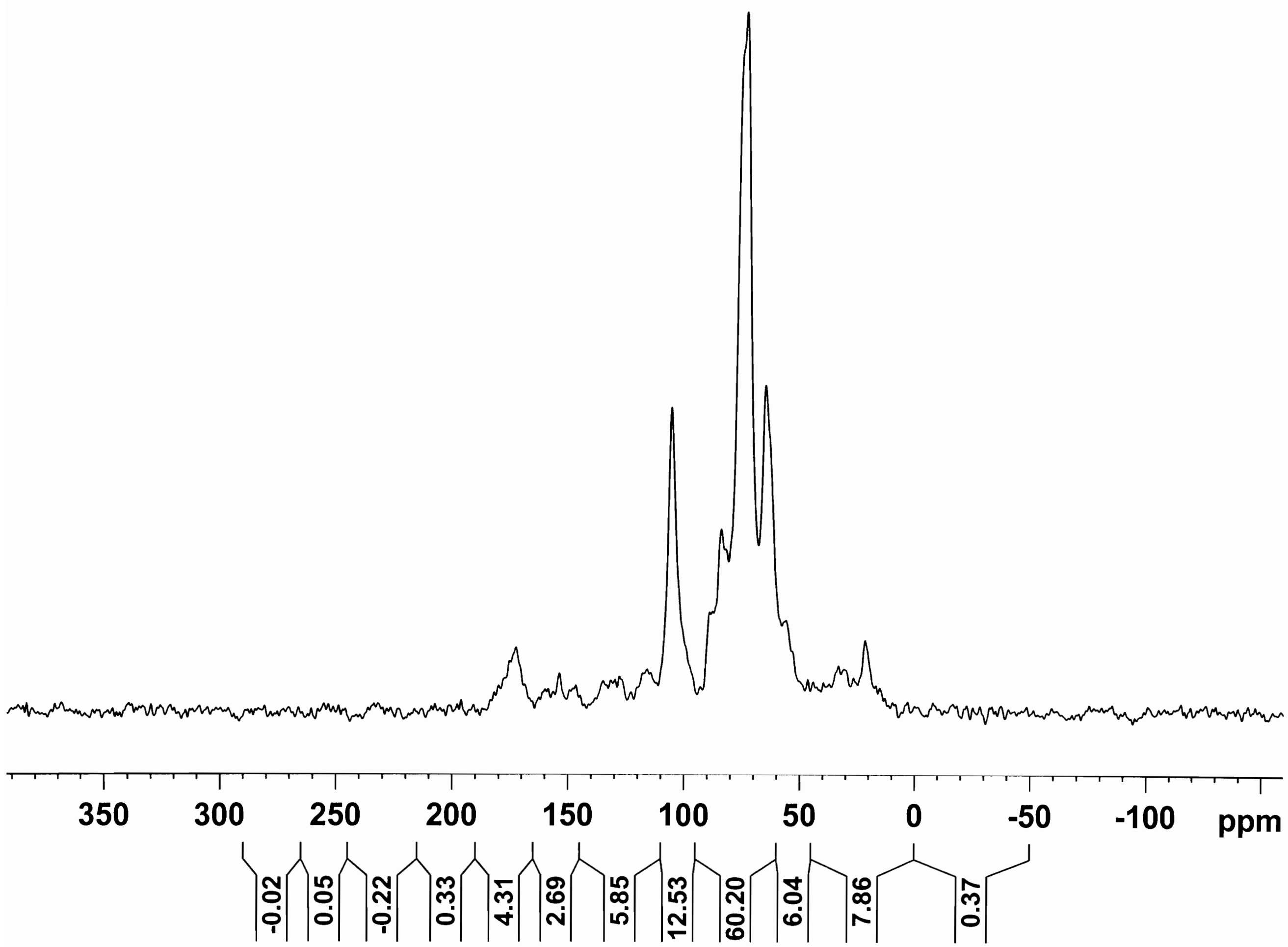
F2 - Acquisition Parameters
Date_ 20091230
Time 15.29
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.0 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 3, No Cover Crop
12/30/2009   59.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters

NAME	KBSNRate_LS302_5B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091230
Time	16.28
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.1 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

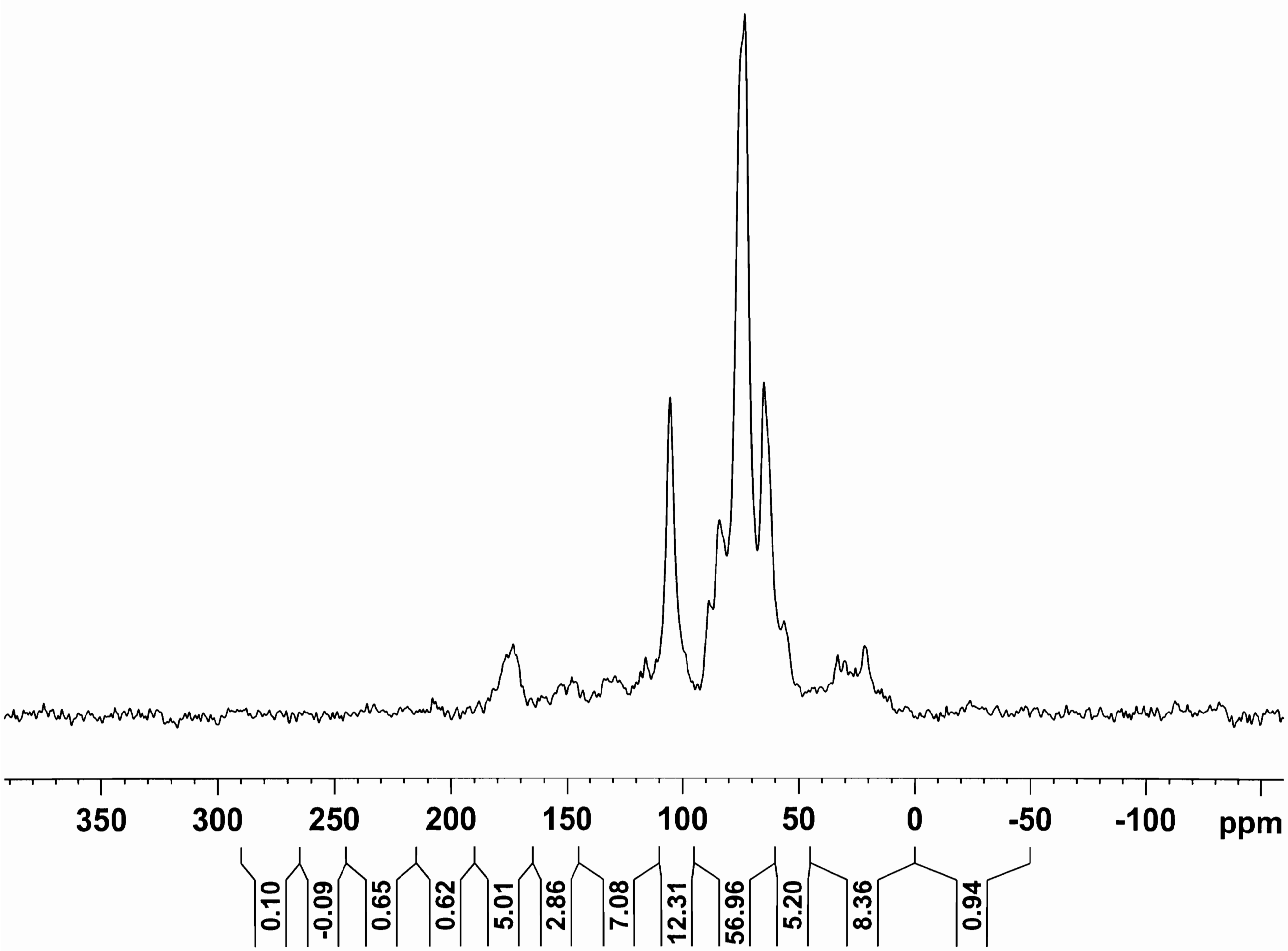
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 4, No Cover Crop
12/30/2009   61.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_LS407_5B
EXPNO 1
PROCNO 1

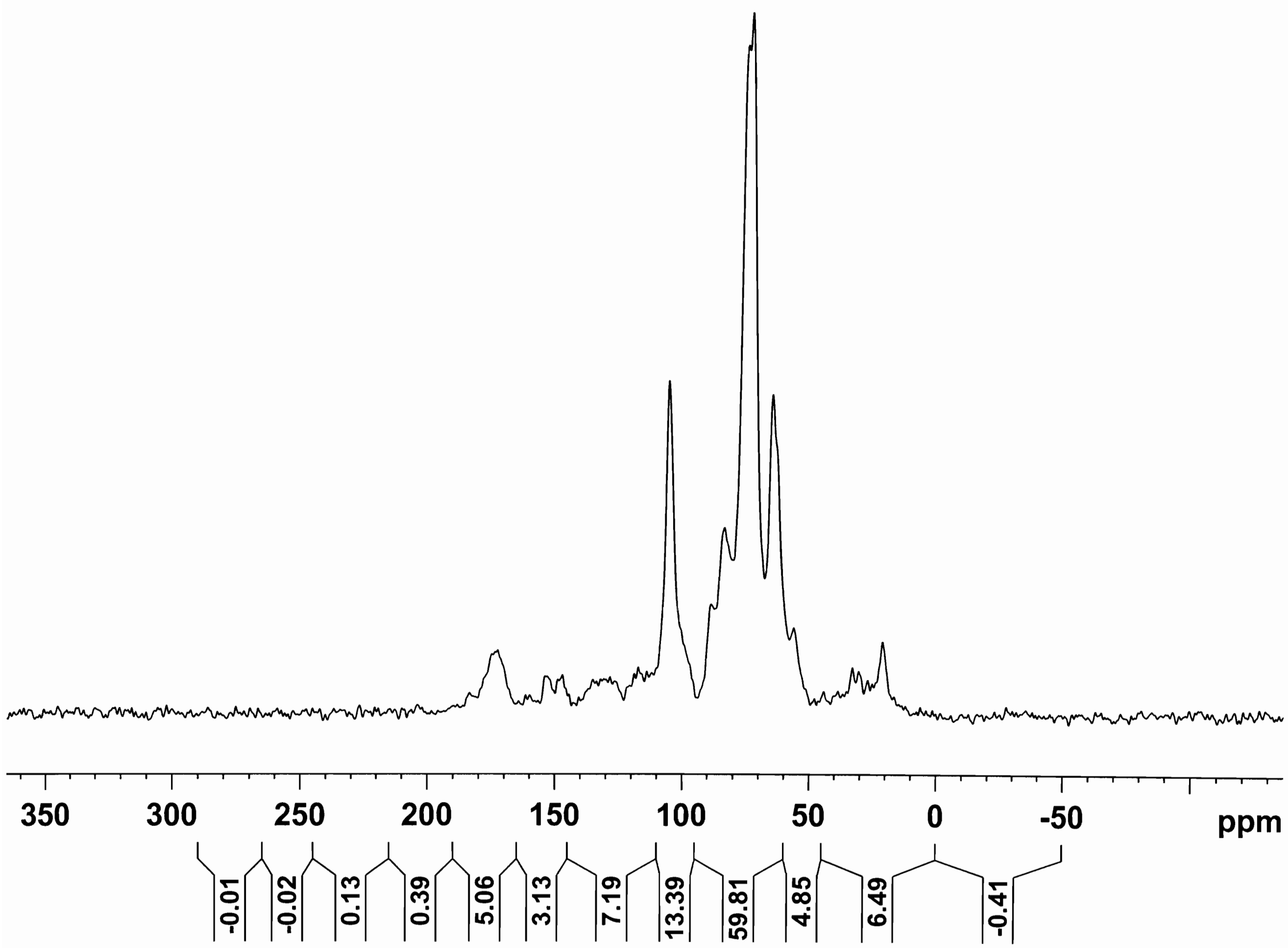
F2 - Acquisition Parameters
Date_ 20091230
Time 17.25
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.1 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/27/2008   56.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME       KBSNRate_LS103_6B
EXPNO                      1
PROCNO                     1

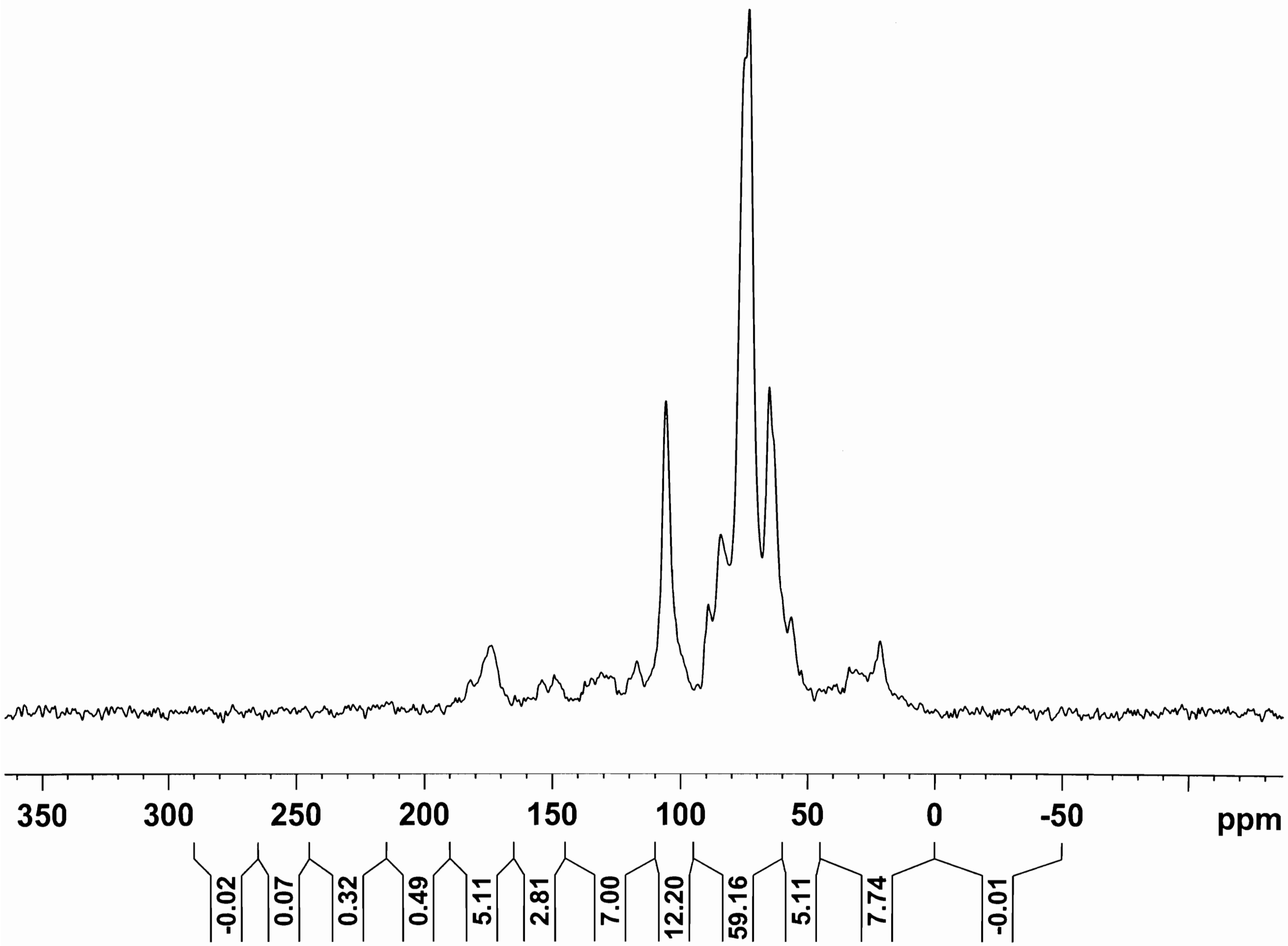
F2 - Acquisition Parameters
Date_               20080627
Time                   16.53
INSTRUM                spect
PROBHD      4 mm MASxvt BB
PULPROG            cp.99.LBA
TD                      1024
SOLVENT
NS                      3500
DS                         0
SWH                25252.525 Hz
FIDRES             24.660669 Hz
AQ                 0.0203450 sec
RG                      2048
DW                    19.800 usec
DE                      6.00 usec
TE                     696.8 K
D1                2.00000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P15                  1000.00 usec
PL1                     1.40 dB
SFO1              50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                      3.20 usec
P31                     5.10 usec
PL2                     6.00 dB
PL12                    3.00 dB
SFO2             200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF                50.3229333 MHz
WDW                       EM
SSB                        0
LB                     30.00 Hz
GB                         0
PC                      1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/15/2008 52.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME KBSNRate_LS105_7B
EXPNO 1
PROCNO 1

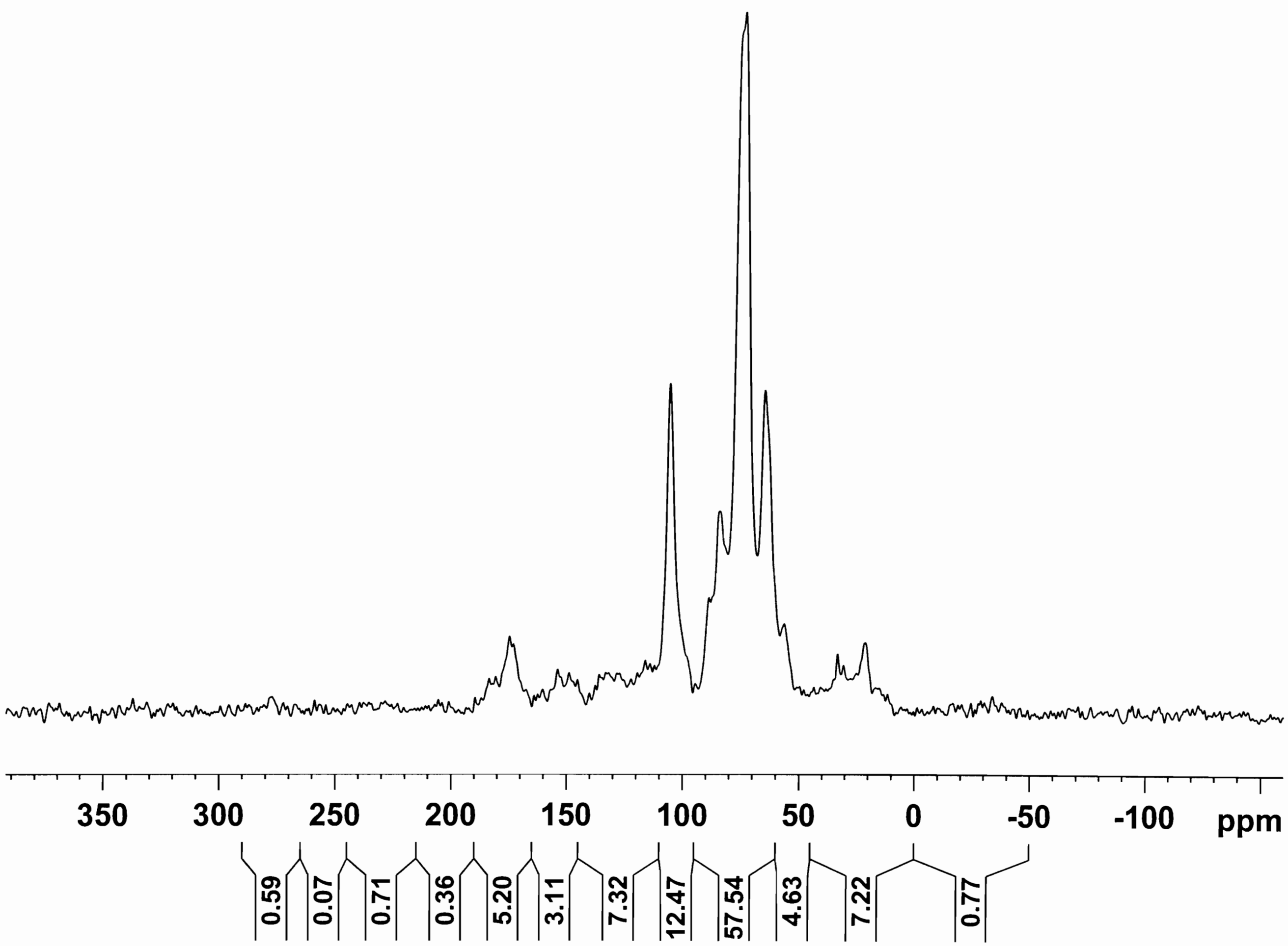
F2 - Acquisition Parameters
Date_ 20080315
Time 19.32
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 3251
DW 19.800 usec
DE 6.00 usec
TE 696.4 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 1.40 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229662 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 2, No Cover Crop
11/11/2009   55.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_LS204_7B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091111
Time	16.31
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1250
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.8 K
D1	3.00000000 sec
TD0	5

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 3, No Cover Crop
11/13/2009   62.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.

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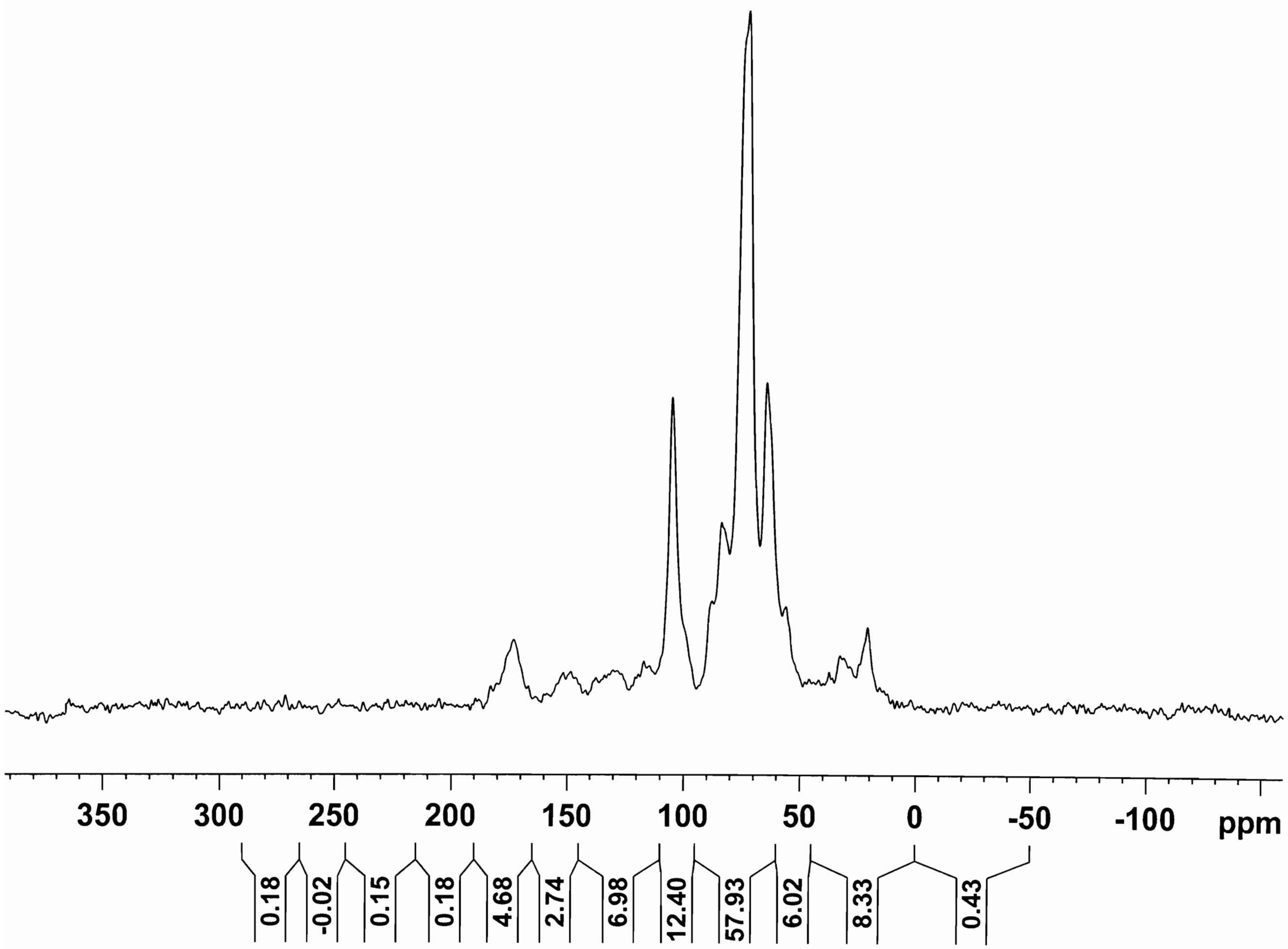


Current Data Parameters

NAME	KBSNRate_LS304_7B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091113
Time	9.12
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.4 K
D1	3.00000000 sec
TD0	8

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

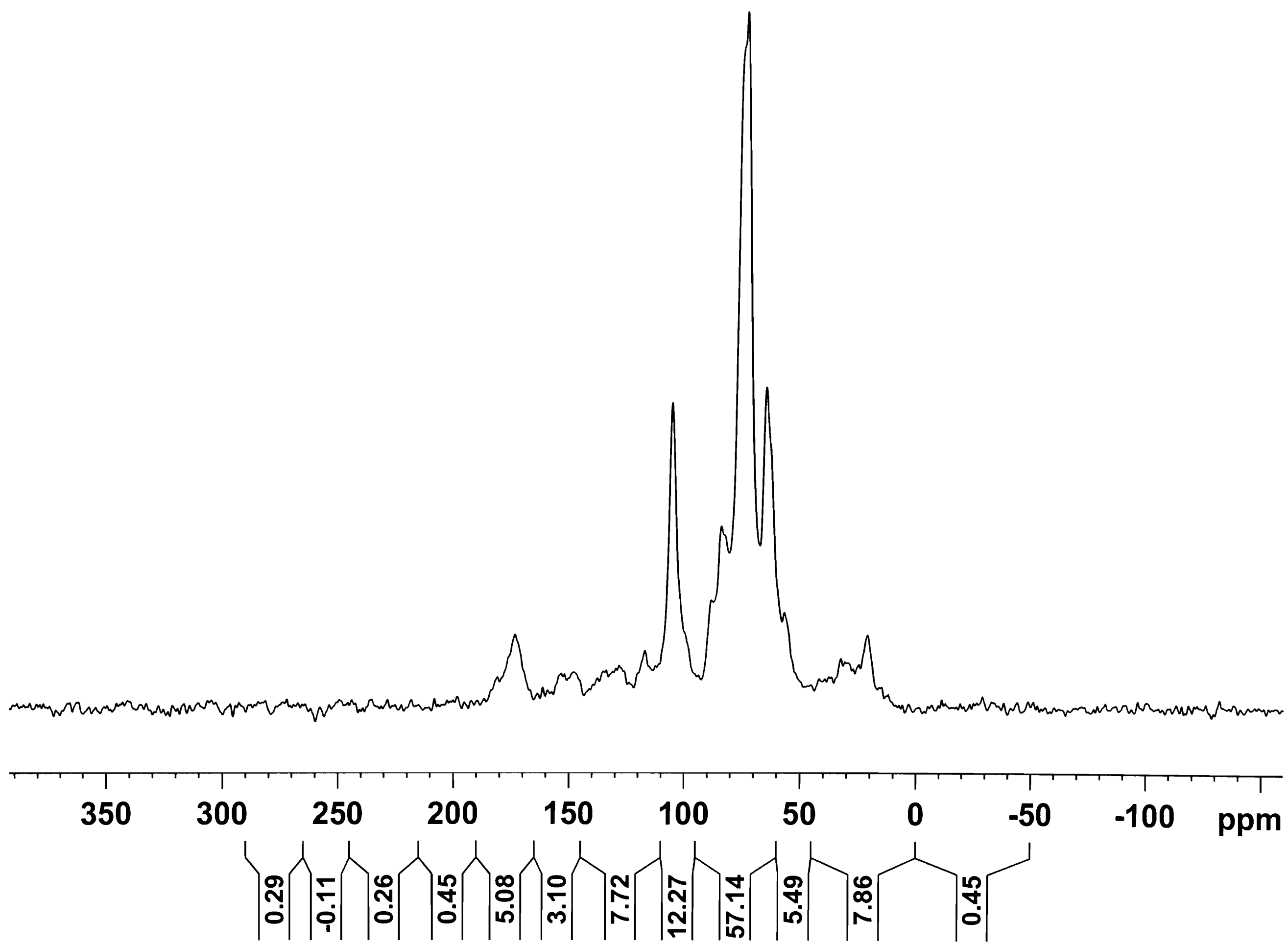
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 4, No Cover Crop
11/12/2009 56.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters

NAME	KBSNRate_LS406_7B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091112
Time	16.51
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.9 K
D1	3.00000000 sec
TD0	8

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

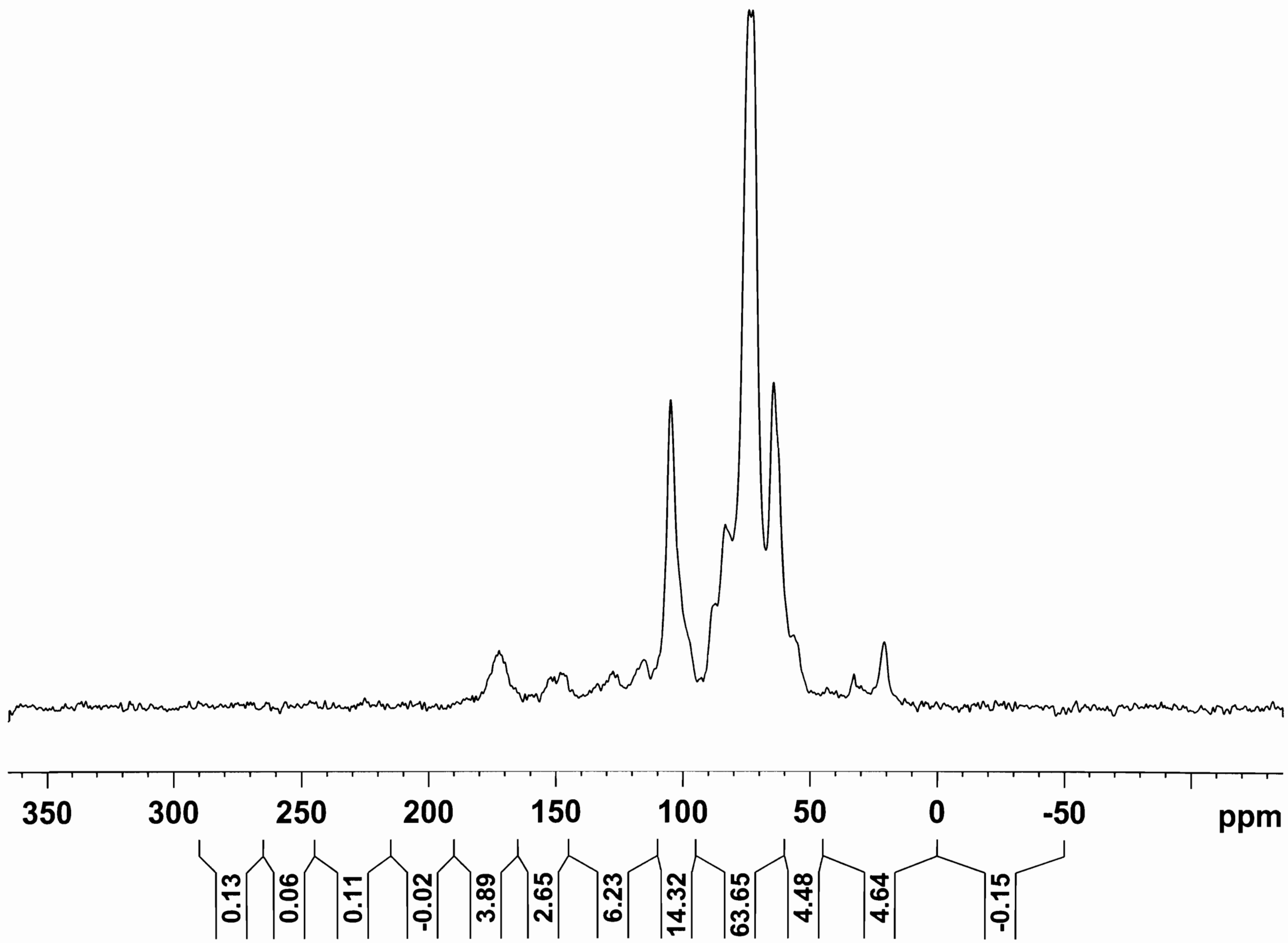
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Rep. Support, Treatment 0 kg N/ha, Replicate 1, Cover Crop
02/13/2008   62.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC101_1A	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20080213	
Time	11.53	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	1625.5	
DW	19.800	usec
DE	6.00	usec
TE	697.6	K
D1	2.00000000	sec

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	1.40	dB
SFO1	50.3287071	MHz

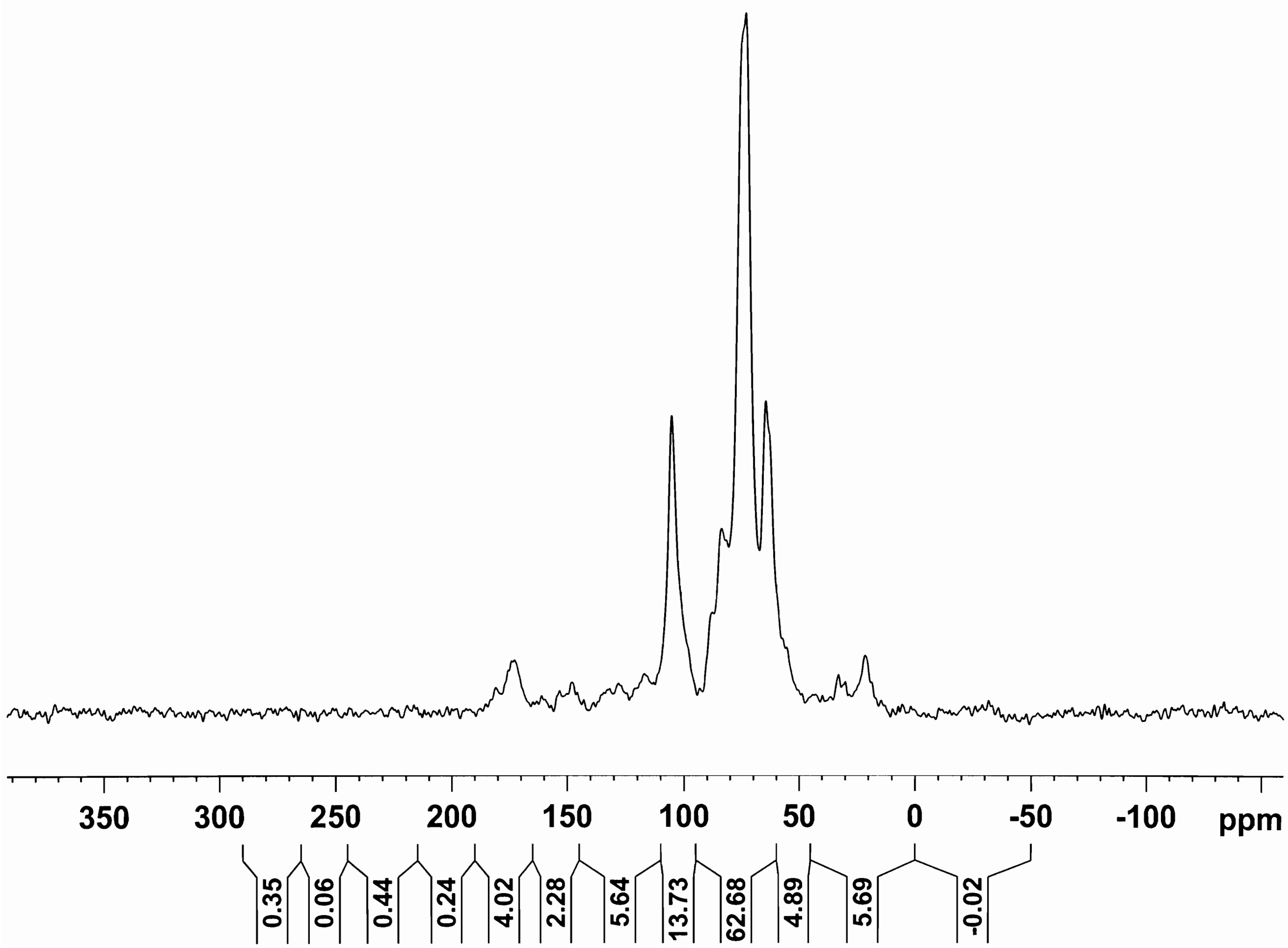
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.10	usec
P31	5.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3229348	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1A Rep. Support, Treatment 0 kg N/ha, Replicate 2, Cover Crop
11/28/2009   69.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME       KBSNRate_HSTC203_1A
EXPNO                        1
PROCNO                       1

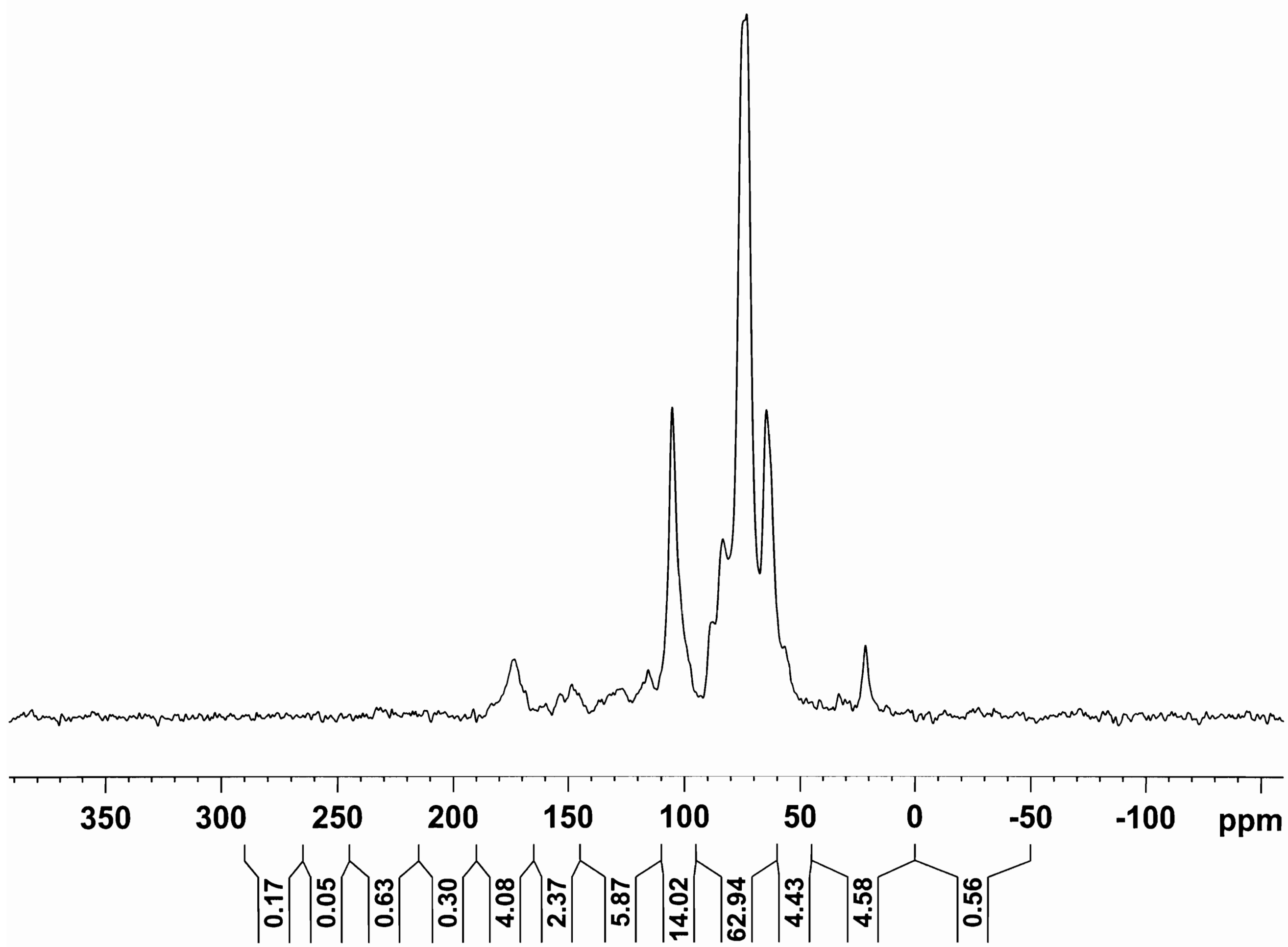
F2 - Acquisition Parameters
Date_              20091128
Time                  13.45
INSTRUM               spect
PROBHD       4 mm MASxvt BB
PULPROG           cp.99.WCH
TD                     1024
SOLVENT
NS                     1000
DS                        0
SWH               27777.777 Hz
FIDRES            27.126736 Hz
AQ                0.0185000 sec
RG                     2048
DW                   18.000 usec
DE                    17.00 usec
TE                    292.2 K
D1               3.00000000 sec
TD0                       4

======== CHANNEL f1 ========
NUC1                    13C
P15                 1000.00 usec
PL1                    2.40 dB
SFO1             50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.15 usec
P31                    6.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3228472 MHz
WDW                      EM
SSB                       0
LB                    40.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1A Rep. Support, Treatment 0 kg N/ha, Replicate 3, Cover Crop
11/28/2009 77.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC307_1A
EXPNO                  1
PROCNO                 1

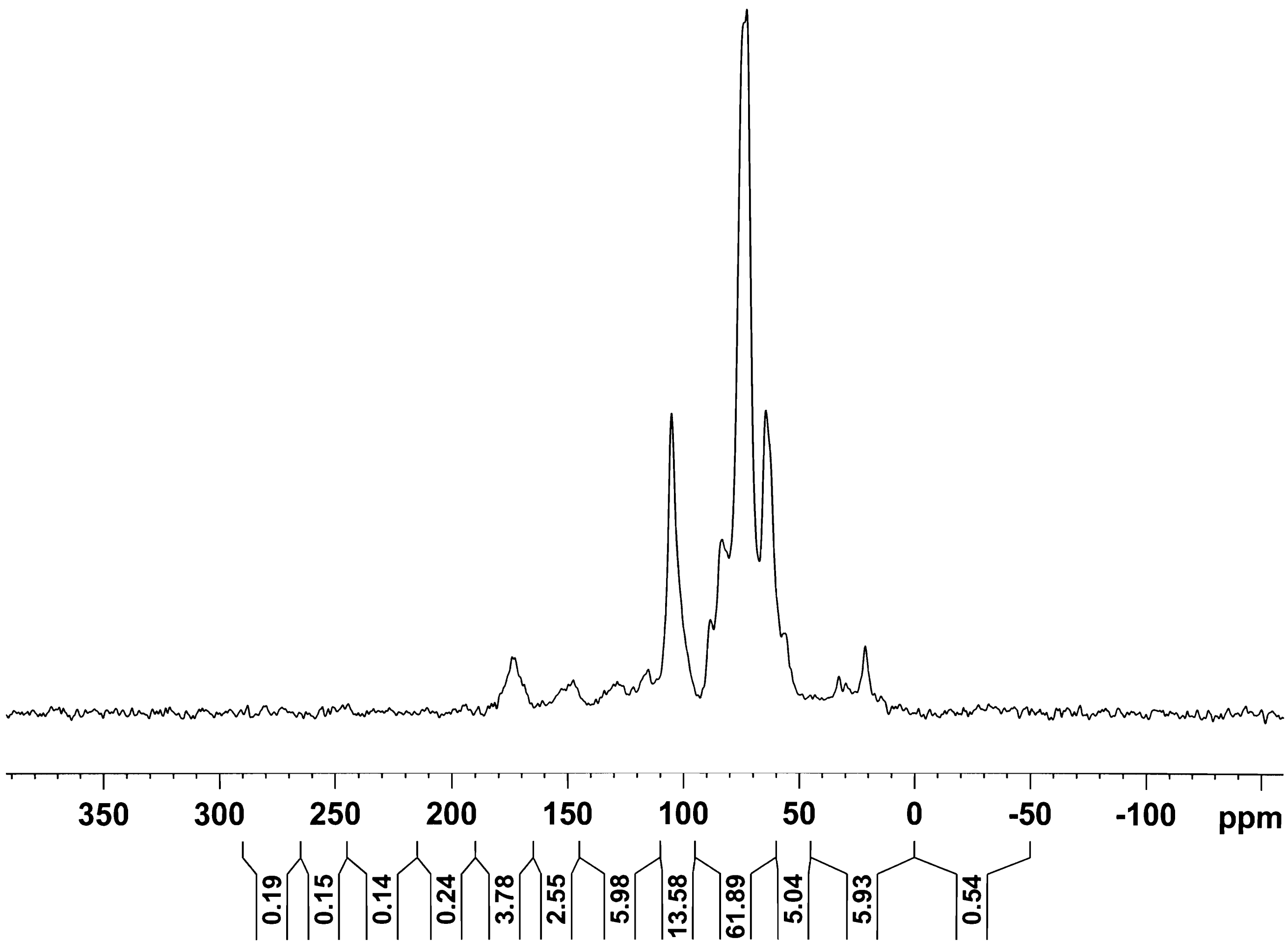
F2 - Acquisition Parameters
Date_             20091128
Time                 15.50
INSTRUM              spect
PROBHD     4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                    1024
SOLVENT
NS                    1000
DS                       0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                    2048
DW                 18.000 usec
DE                  17.00 usec
TE                  292.2 K
D1             3.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   13C
P15               1000.00 usec
PL1                  2.40 dB
SFO1           50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.15 usec
P31                  6.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3228472 MHz
WDW                    EM
SSB                     0
LB                  40.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1A Rep. Support, Treatment 0 kg N/ha, Replicate 4, Cover Crop
11/28/2009   76.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_HSTC402_1A
EXPNO 1
PROCNO 1

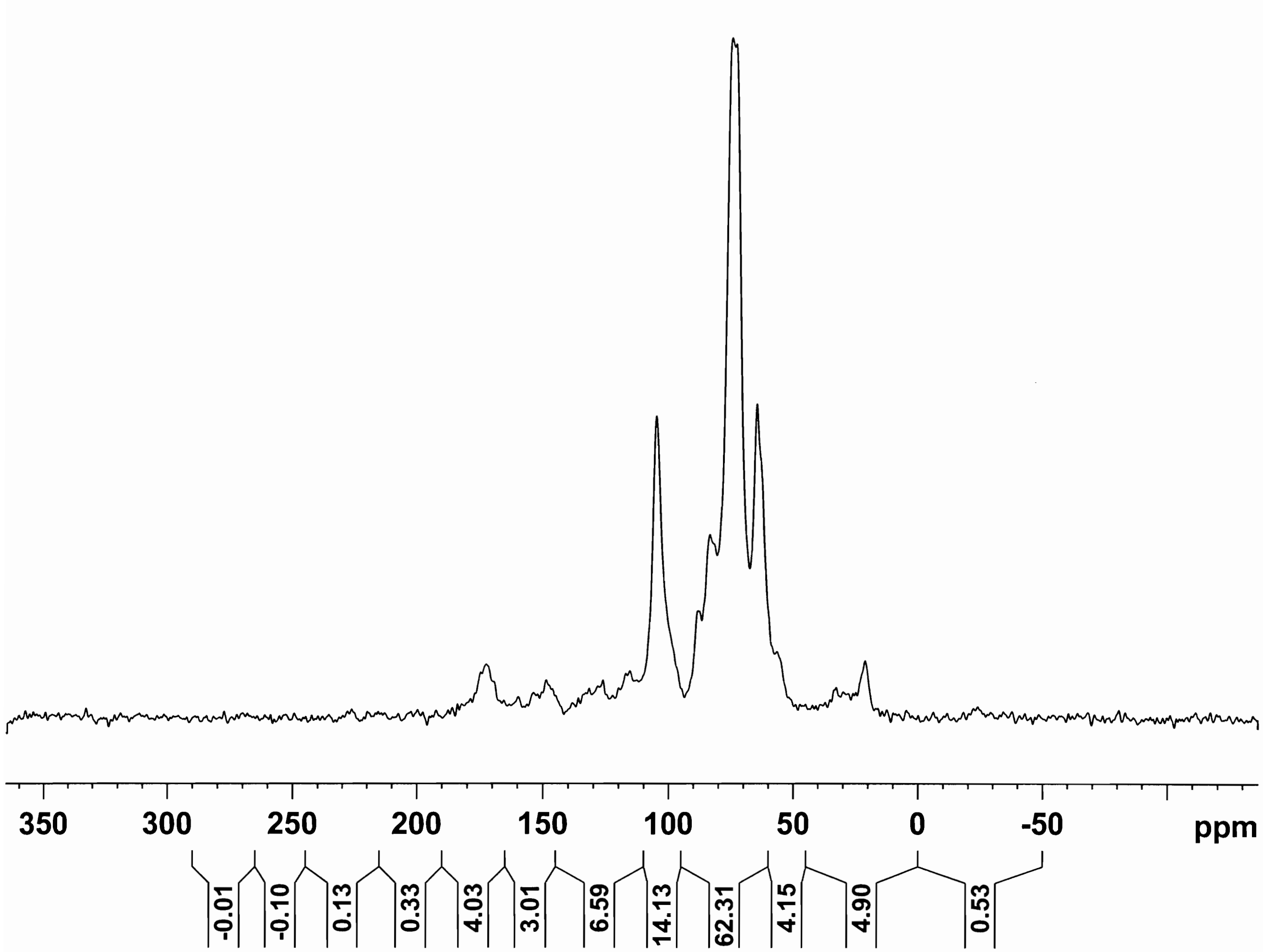
F2 - Acquisition Parameters
Date_ 20091128
Time 17.46
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.2 K
D1 3.00000000 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Rep. Support, Treatment 34 kg N/ha, Replicate 1, Cover Crop
02/14/2008   57.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC107_2A
EXPNO                      1
PROCNO                     1

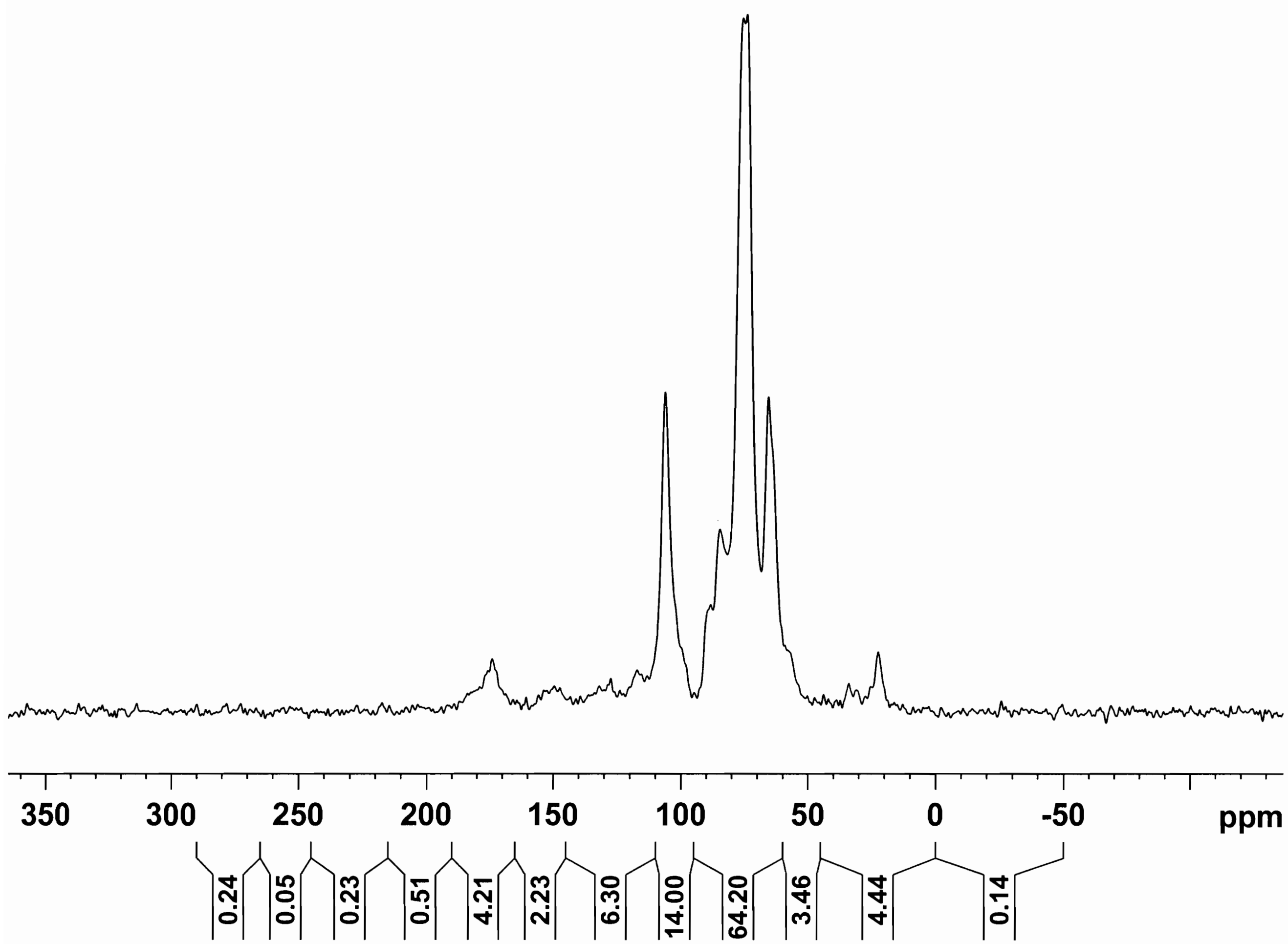
F2 - Acquisition Parameters
Date_              20080214
Time                  17.41
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                 2896.3
DW                 19.800 usec
DE                   6.00 usec
TE                  696.2 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.10 usec
P31                   5.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229348 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Rep. Support, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/10/2008   58.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_HSTC106_3A
EXPNO                    1
PROCNO                   1

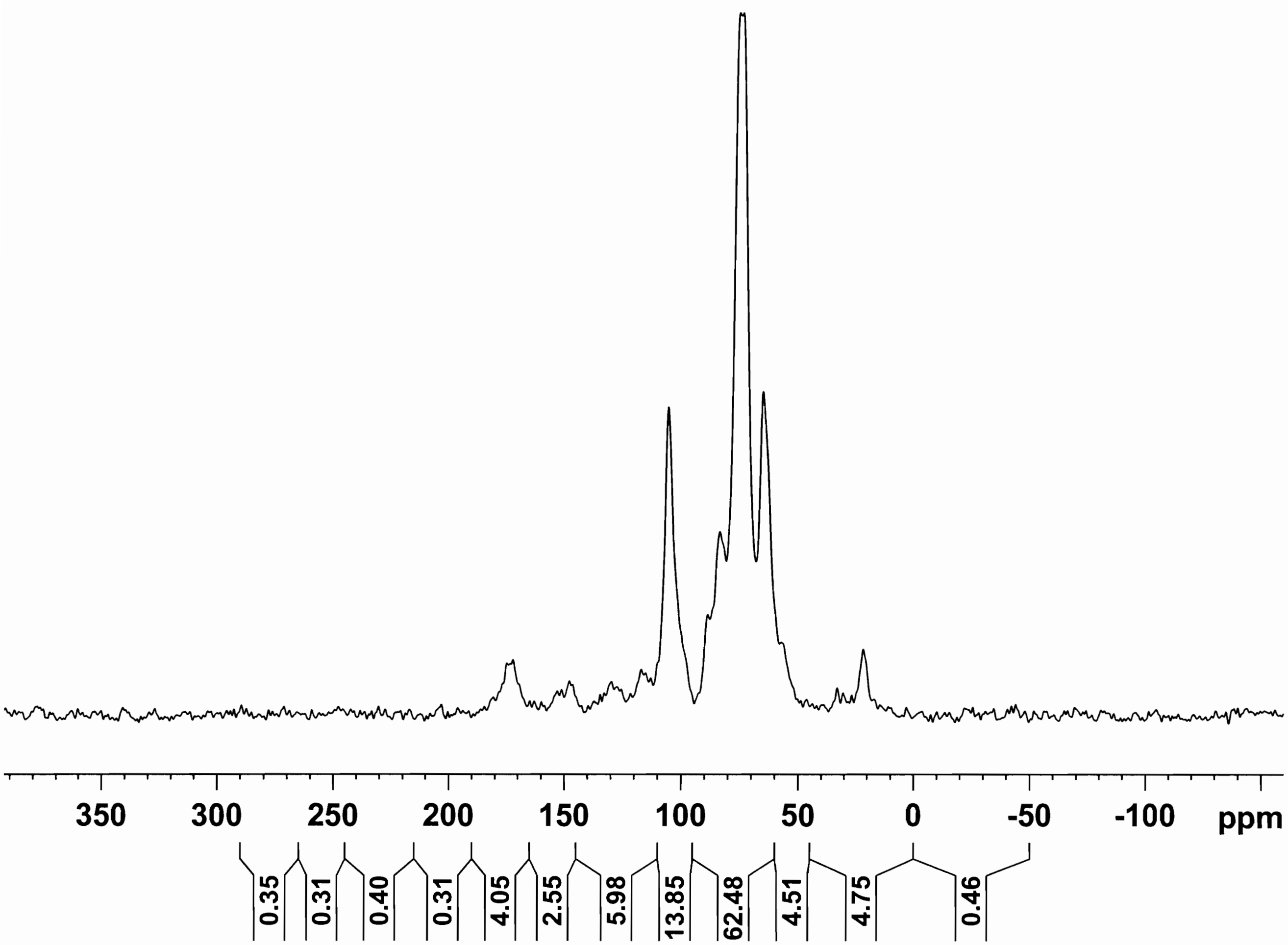
F2 - Acquisition Parameters
Date_             20080310
Time                 10.42
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                  1625.5
DW                  19.800 usec
DE                    6.00 usec
TE                   694.7 K
D1              2.00000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   1.40 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.05 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229662 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3A Rep. Support, Treatment 67 kg N/ha, Replicate 2, Cover Crop
11/28/2009 71.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC202_3A	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20091128	
Time	9.55	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	292.1	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

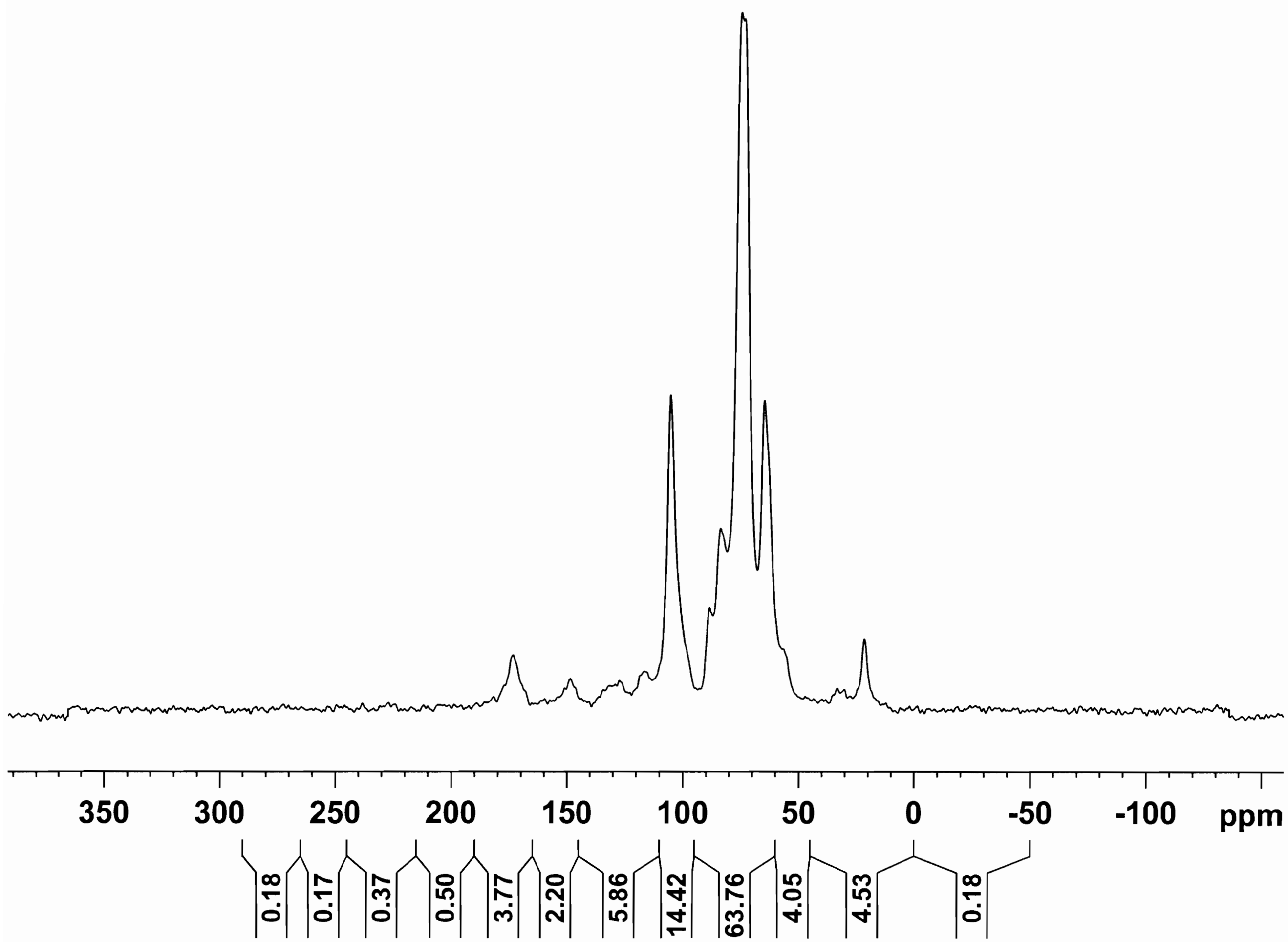
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3A Rep. Support, Treatment 67 kg N/ha, Replicate 3, Cover Crop
11/15/2009   76.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters
NAME   KBSNRate_HSTC305_3A
EXPNO   1
PROCNO   1

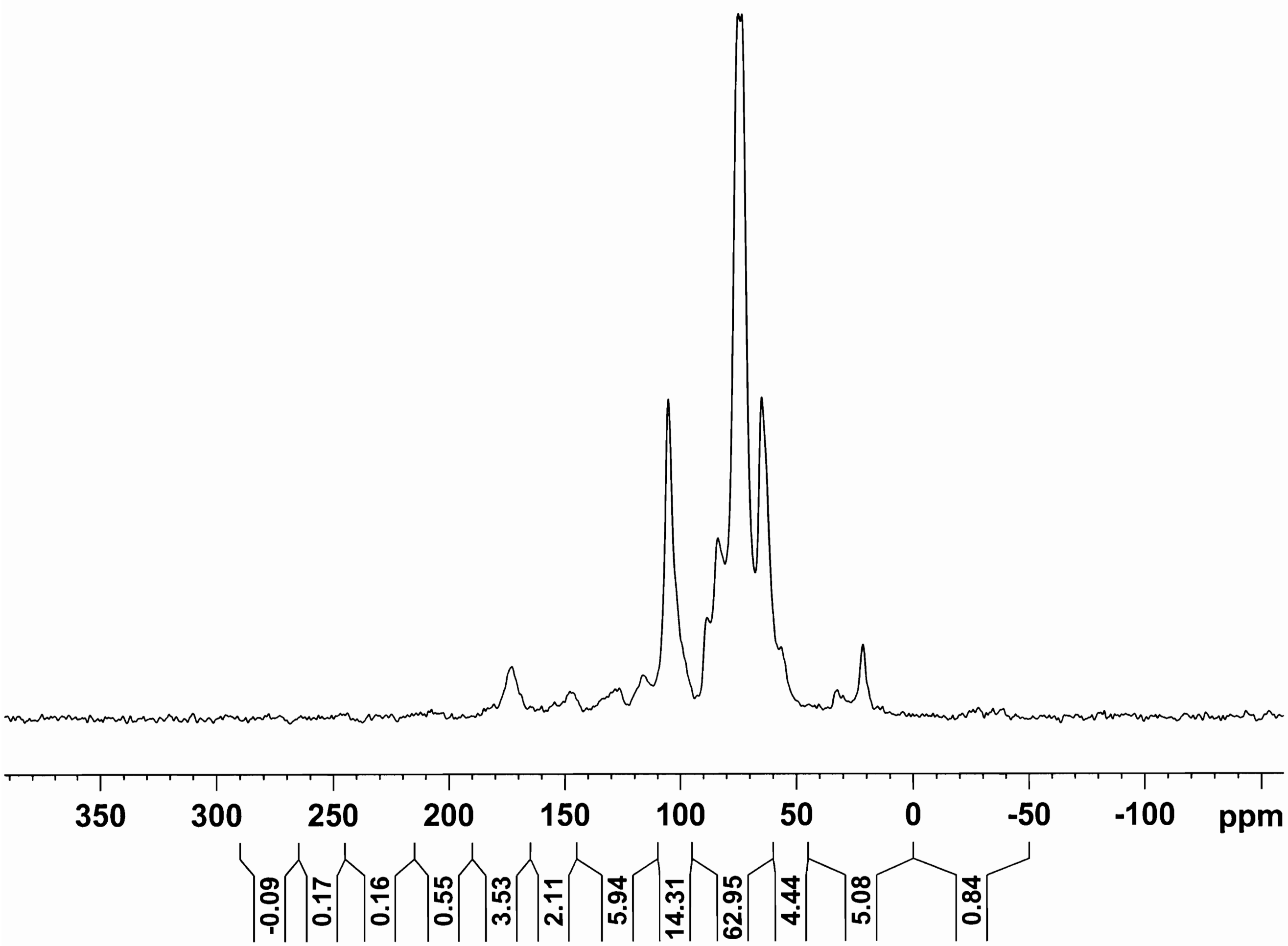
F2 - Acquisition Parameters
Date_   20091115
Time   20.23
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.WCH
TD   1024
SOLVENT
NS   2000
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   17.00 usec
TE   292.3 K
D1   3.00000000 sec
TD0   8

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   2.40 dB
SFO1   50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.15 usec
P31   6.00 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3228472 MHz
WDW   EM
SSB   0
LB   40.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3A Rep. Support, Treatment 67 kg N/ha, Replicate 4, Cover Crop
11/15/2009   72.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC404_3A
EXPNO                     1
PROCNO                    1

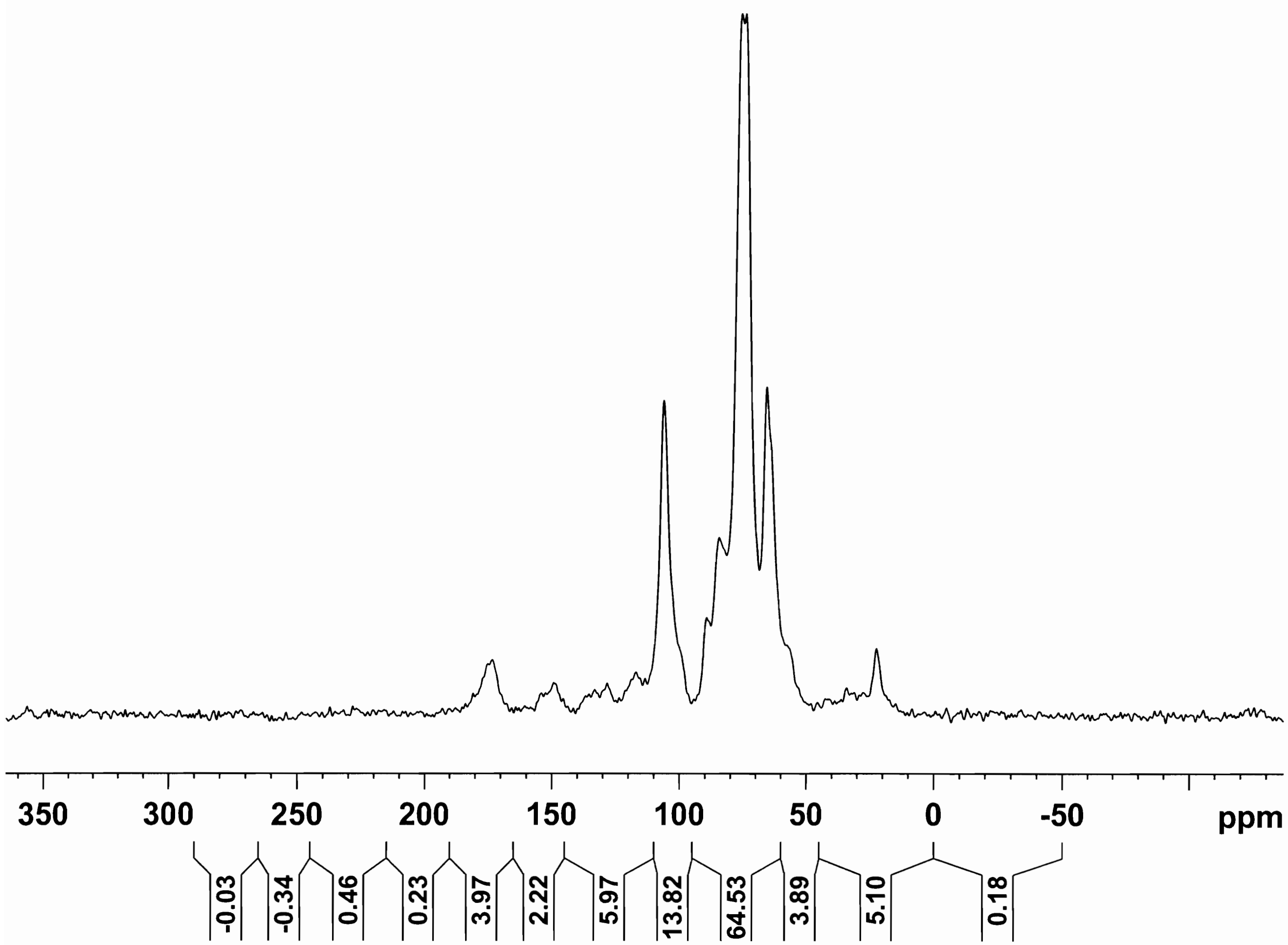
F2 - Acquisition Parameters
Date_          20091115
Time              15.37
INSTRUM           spect
PROBHD   4 mm MASxvt BB
PULPROG       cp.99.WCH
TD                 1024
SOLVENT
NS                 2000
DS                    0
SWH           27777.777 Hz
FIDRES        27.126736 Hz
AQ            0.0185000 sec
RG                 2048
DW               18.000 usec
DE                17.00 usec
TE                292.4 K
D1           3.00000000 sec
TD0                   8

======== CHANNEL f1 ========
NUC1                13C
P15             1000.00 usec
PL1                2.40 dB
SFO1         50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2          tppm15
NUC2                 1H
P3                 3.15 usec
P31                6.00 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                16384
SF           50.3228472 MHz
WDW                  EM
SSB                   0
LB                40.00 Hz
GB                    0
PC                 1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Rep. Support, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/10/2008   65.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC102_4A
EXPNO                      1
PROCNO                     1

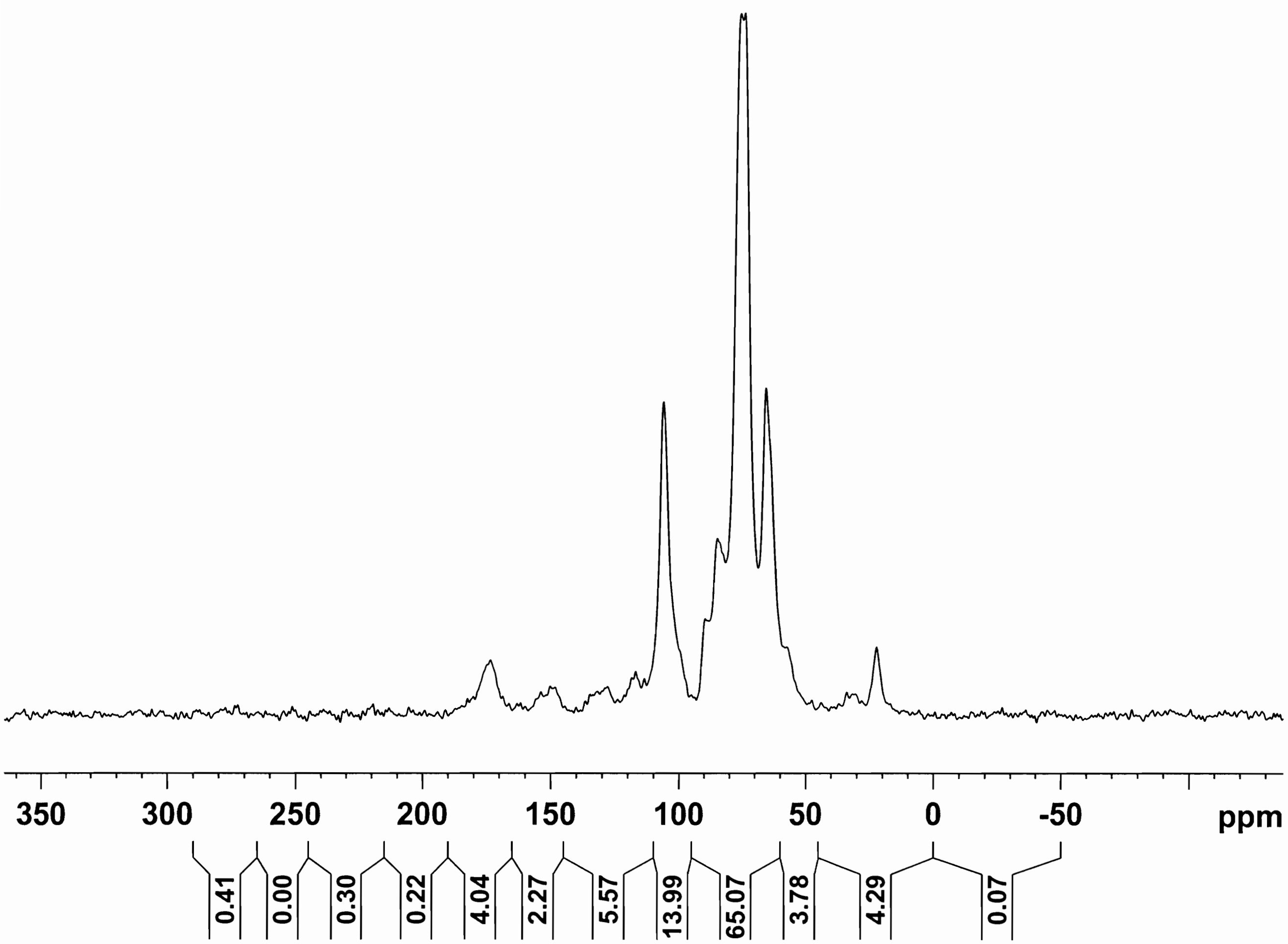
F2 - Acquisition Parameters
Date_               20080310
Time                   13.36
INSTRUM                spect
PROBHD   4 mm MASxvt BB
PULPROG          cp.99.LBA
TD                      1024
SOLVENT
NS                      3500
DS                         0
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                    2580.3
DW                19.800 usec
DE                  6.00 usec
TE                 694.8 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P15              1000.00 usec
PL1                  1.40 dB
SFO1          50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                      1H
P3                  3.05 usec
P31                 5.10 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF            50.3229662 MHz
WDW                       EM
SSB                        0
LB                  30.00 Hz
GB                         0
PC                      1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Rep. Support, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/10/2008   67.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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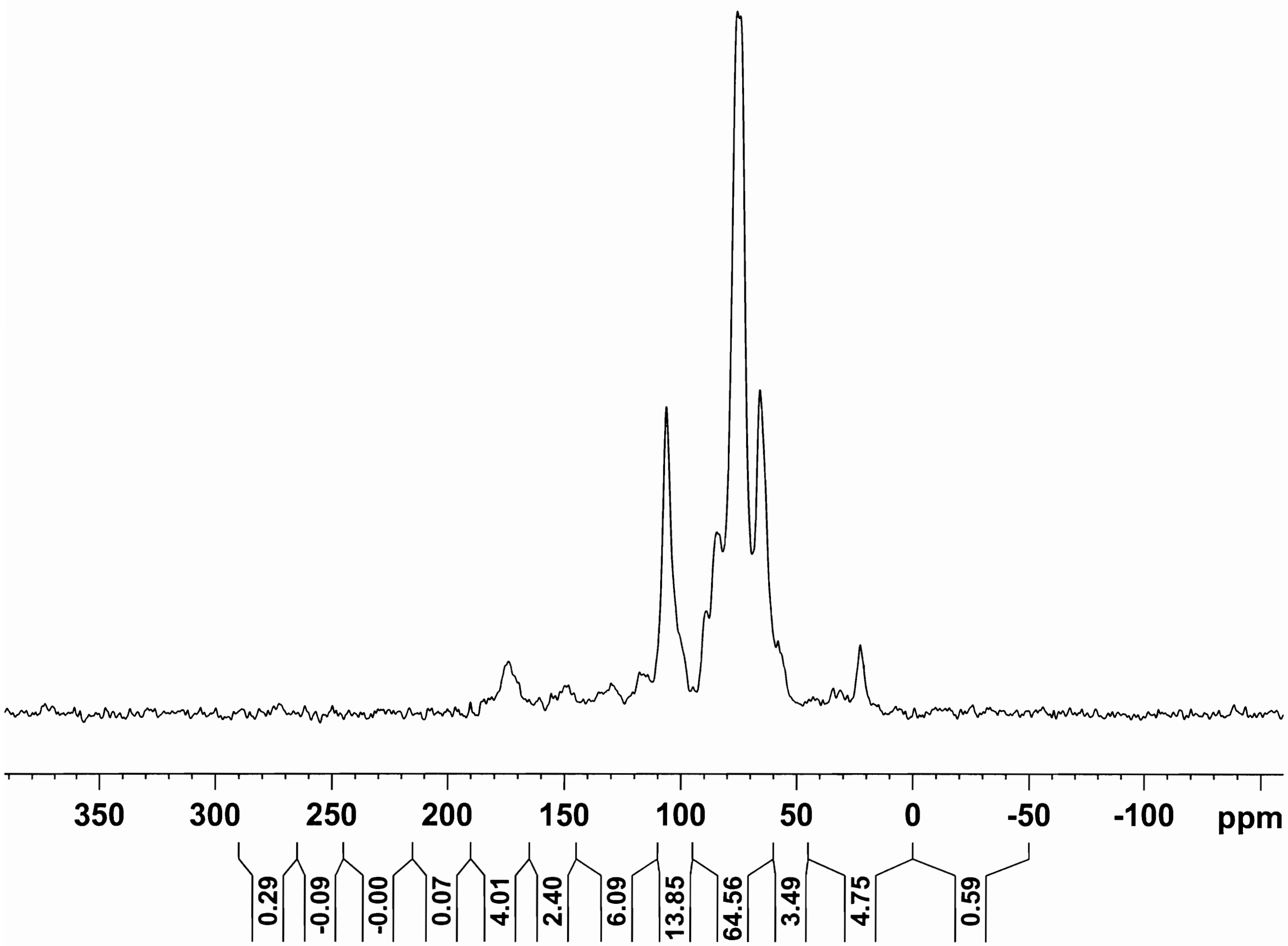
Current Data Parameters		
NAME	KBSNRate_HSTC104_5A	
EXPNO	1	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20080310	
Time	17.04	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	4597.6	
DW	19.800	usec
DE	6.00	usec
TE	694.8	K
D1	2.00000000	sec
======== CHANNEL f1 ========		
NUC1	13C	
P15	1000.00	usec
PL1	1.40	dB
SFO1	50.3287071	MHz
======== CHANNEL f2 ========		
CPDPRG2	tppm15	
NUC2	1H	
P3	3.05	usec
P31	5.10	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz
F2 - Processing parameters		
SI	16384	
SF	50.3229662	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5A Rep. Support, Treatment 134 kg N/ha, Replicate 2, Cover Crop
01/04/2010 74.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

Current Data Parameters

NAME	KBSNRate_HSTC205_5A	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20100104	
Time	17.28	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cp.99.WCH	
TD	1024	
SOLVENT		
NS	1000	
DS	0	
SWH	27777.777	Hz
FIDRES	27.126736	Hz
AQ	0.0185000	sec
RG	2048	
DW	18.000	usec
DE	17.00	usec
TE	292.0	K
D1	3.00000000	sec
TD0	4	

======== CHANNEL f1 ========

NUC1	13C	
P15	1000.00	usec
PL1	2.40	dB
SFO1	50.3287070	MHz

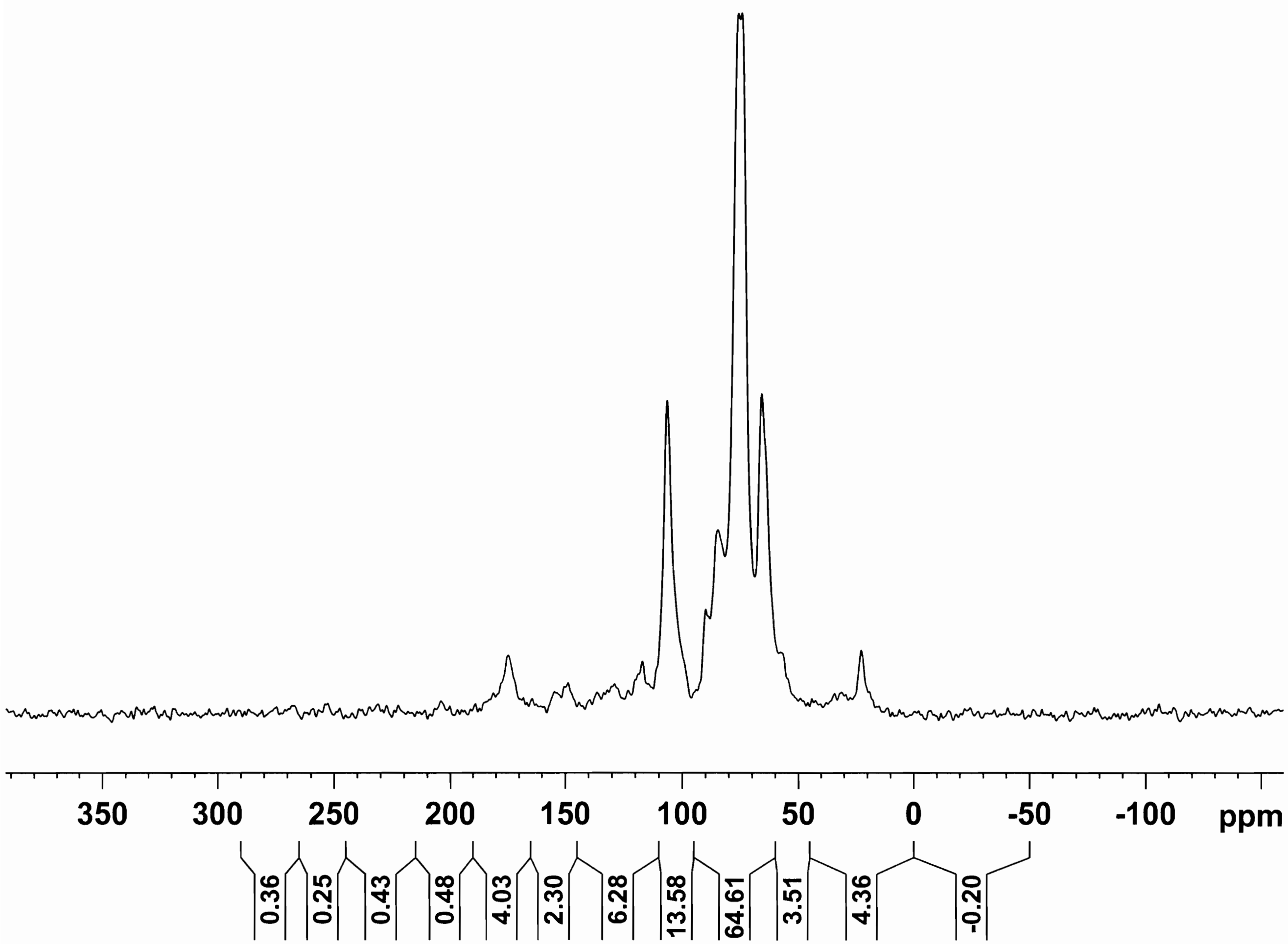
======== CHANNEL f2 ========

CPDPRG2	tppm15	
NUC2	1H	
P3	3.15	usec
P31	6.00	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3228472	MHz
WDW	EM	
SSB	0	
LB	40.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5A Rep. Support, Treatment 134 kg N/ha, Replicate 3, Cover Crop
01/04/2010   73.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

```
Current Data Parameters
NAME     KBSNRate_HSTC302_5A
EXPNO                  1
PROCNO                 1

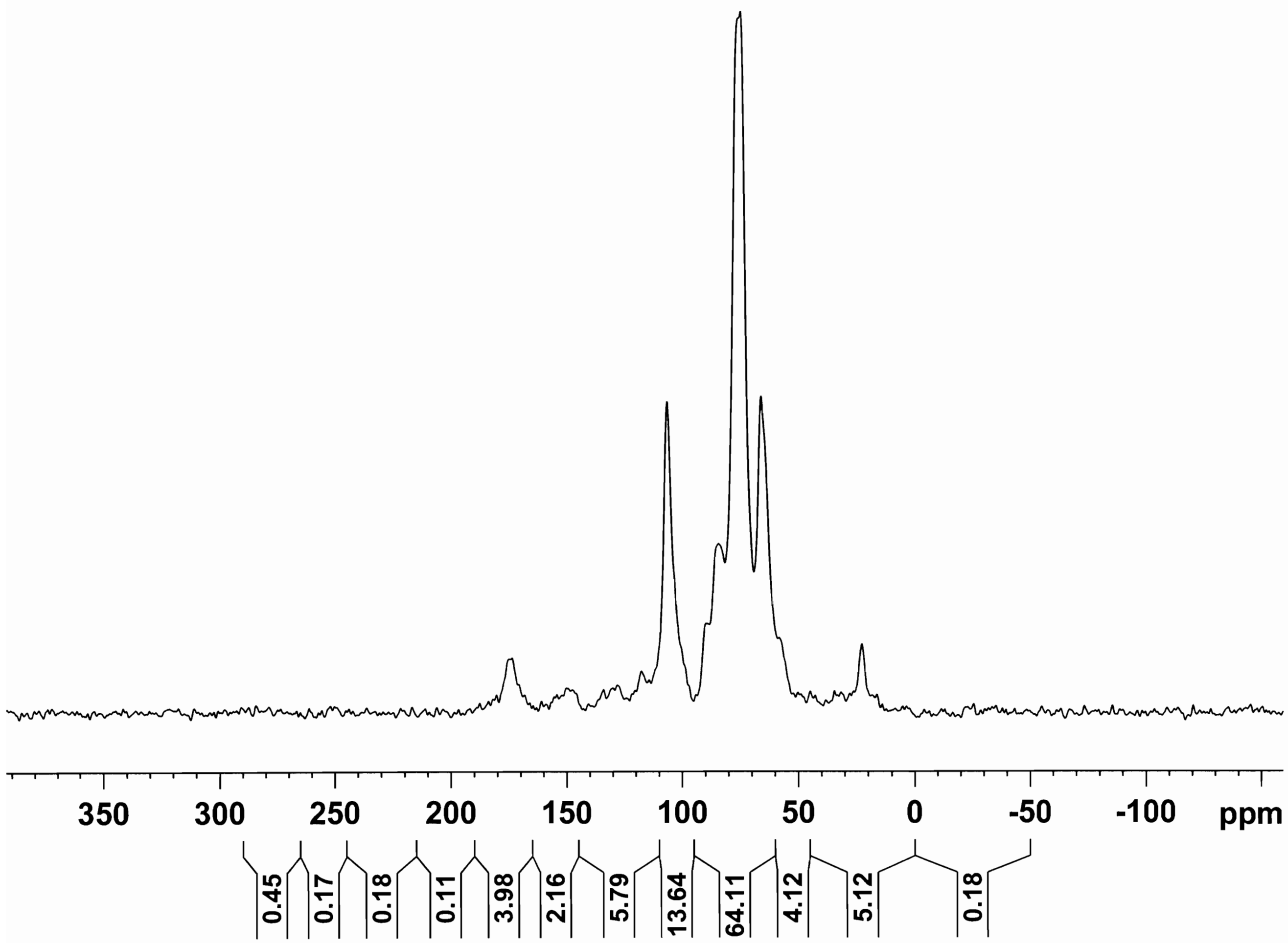
F2 - Acquisition Parameters
Date_           20100104
Time               19.12
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                 1024
SOLVENT
NS                 1000
DS                    0
SWH           27777.777 Hz
FIDRES        27.126736 Hz
AQ            0.0185000 sec
RG                 2048
DW               18.000 usec
DE                17.00 usec
TE                291.9 K
D1           3.00000000 sec
TD0                   4

======== CHANNEL f1 ========
NUC1                13C
P15             1000.00 usec
PL1                2.40 dB
SFO1         50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2          tppm15
NUC2                 1H
P3                 3.15 usec
P31                6.00 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                16384
SF           50.3228472 MHz
WDW                  EM
SSB                   0
LB                40.00 Hz
GB                    0
PC                 1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5A Rep. Support, Treatment 134 kg N/ha, Replicate 4, Cover Crop
01/04/2010   77.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC407_5A
EXPNO                      1
PROCNO                     1

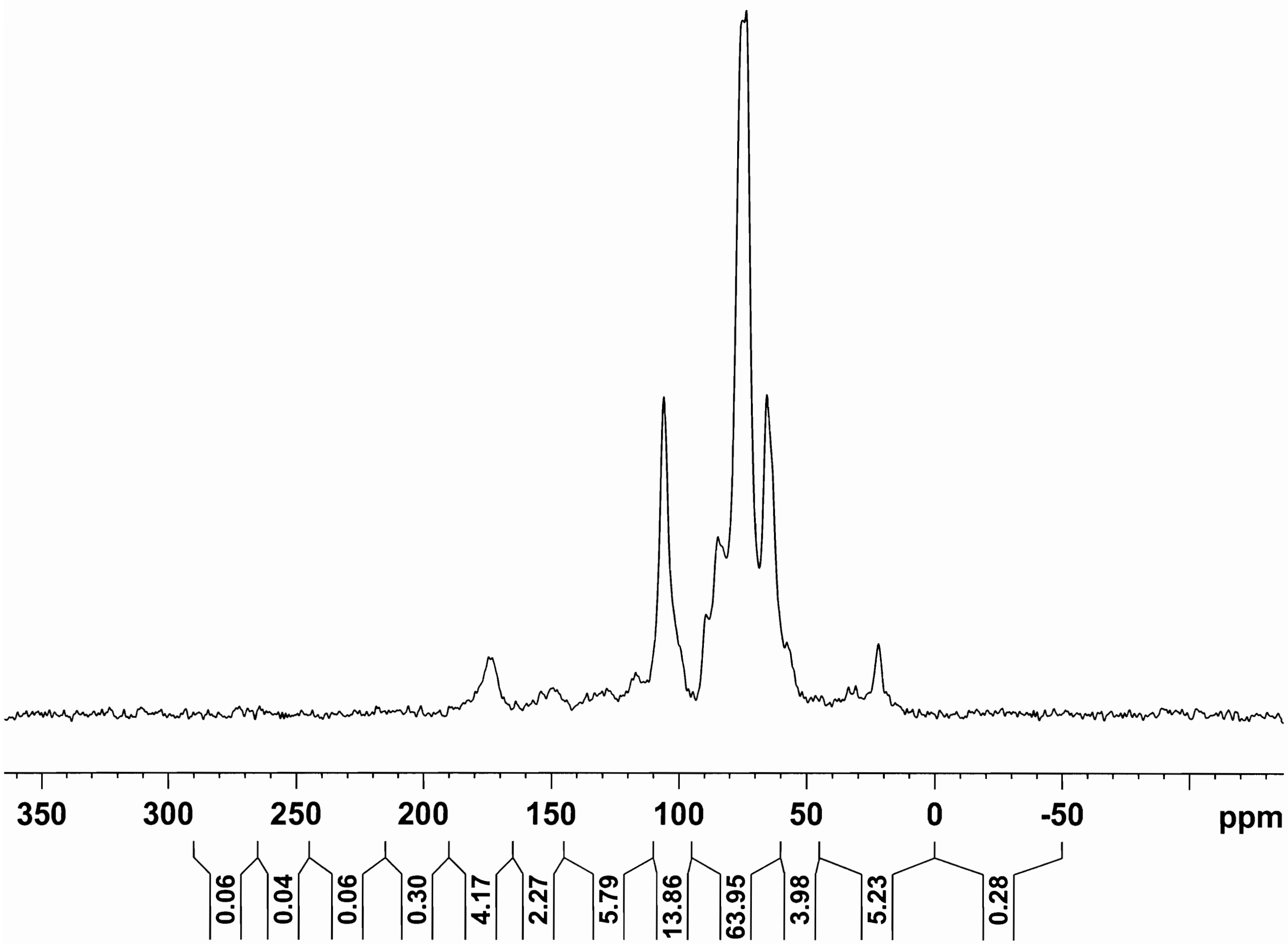
F2 - Acquisition Parameters
Date_               20100104
Time                   20.08
INSTRUM                spect
PROBHD   4 mm MASxvt BB
PULPROG           cp.99.WCH
TD                      1024
SOLVENT
NS                      1000
DS                         0
SWH                27777.777 Hz
FIDRES             27.126736 Hz
AQ                 0.0185000 sec
RG                      2048
DW                    18.000 usec
DE                     17.00 usec
TE                     291.8 K
D1                3.00000000 sec
TD0                        4

======== CHANNEL f1 ========
NUC1                     13C
P15                  1000.00 usec
PL1                     2.40 dB
SFO1              50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                      3.15 usec
P31                     6.00 usec
PL2                     6.00 dB
PL12                    3.00 dB
SFO2             200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF                50.3228472 MHz
WDW                       EM
SSB                        0
LB                     40.00 Hz
GB                         0
PC                      1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Rep. Support, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/11/2008 58.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC103_6A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080311
Time	12.35
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2298.8
DW	19.800 usec
DE	6.00 usec
TE	694.4 K
D1	2.00000000 sec

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz

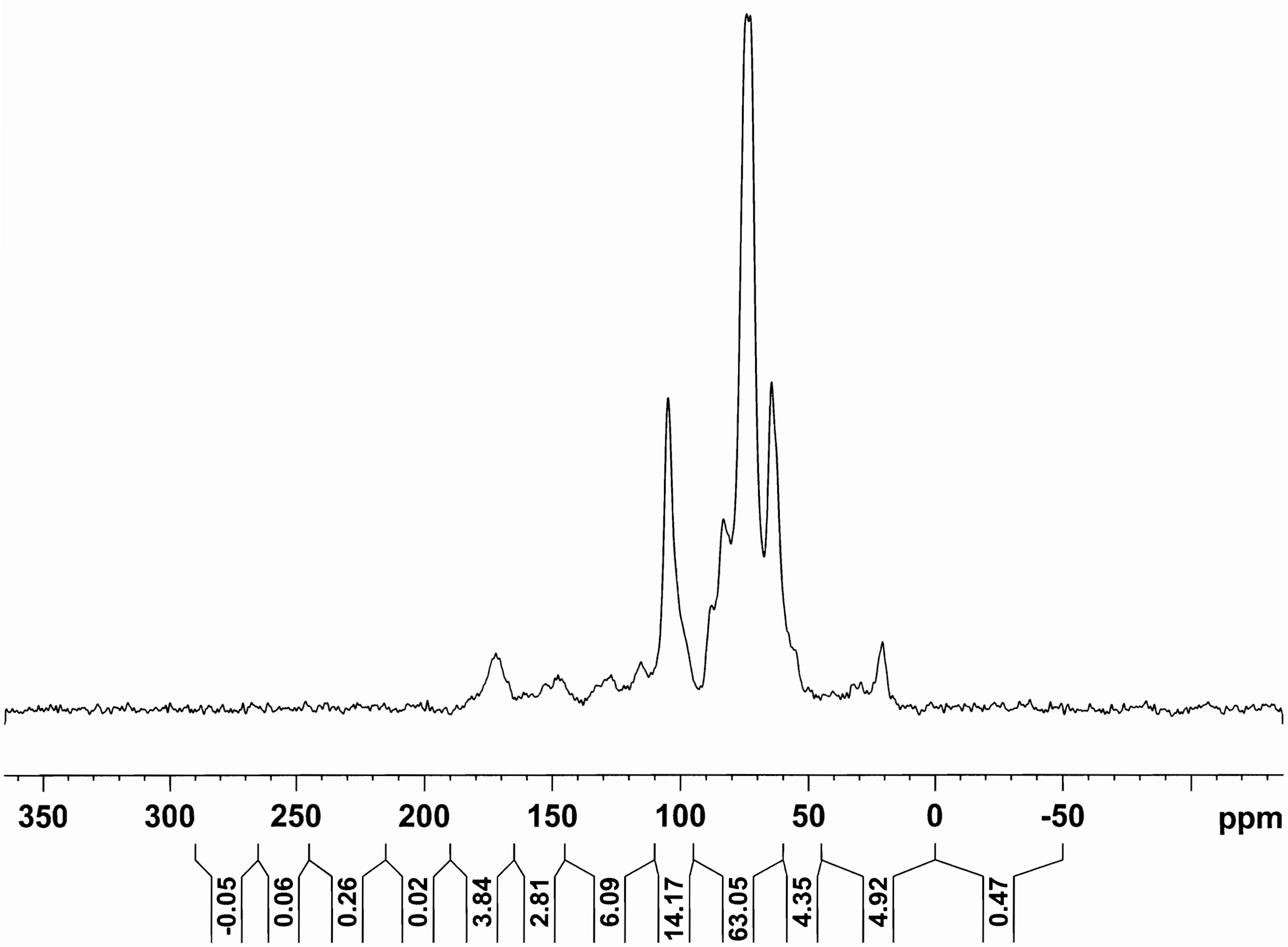
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229662 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Rep. Support, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/14/2008   58.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_HSTC105_7A
EXPNO                   1
PROCNO                  1

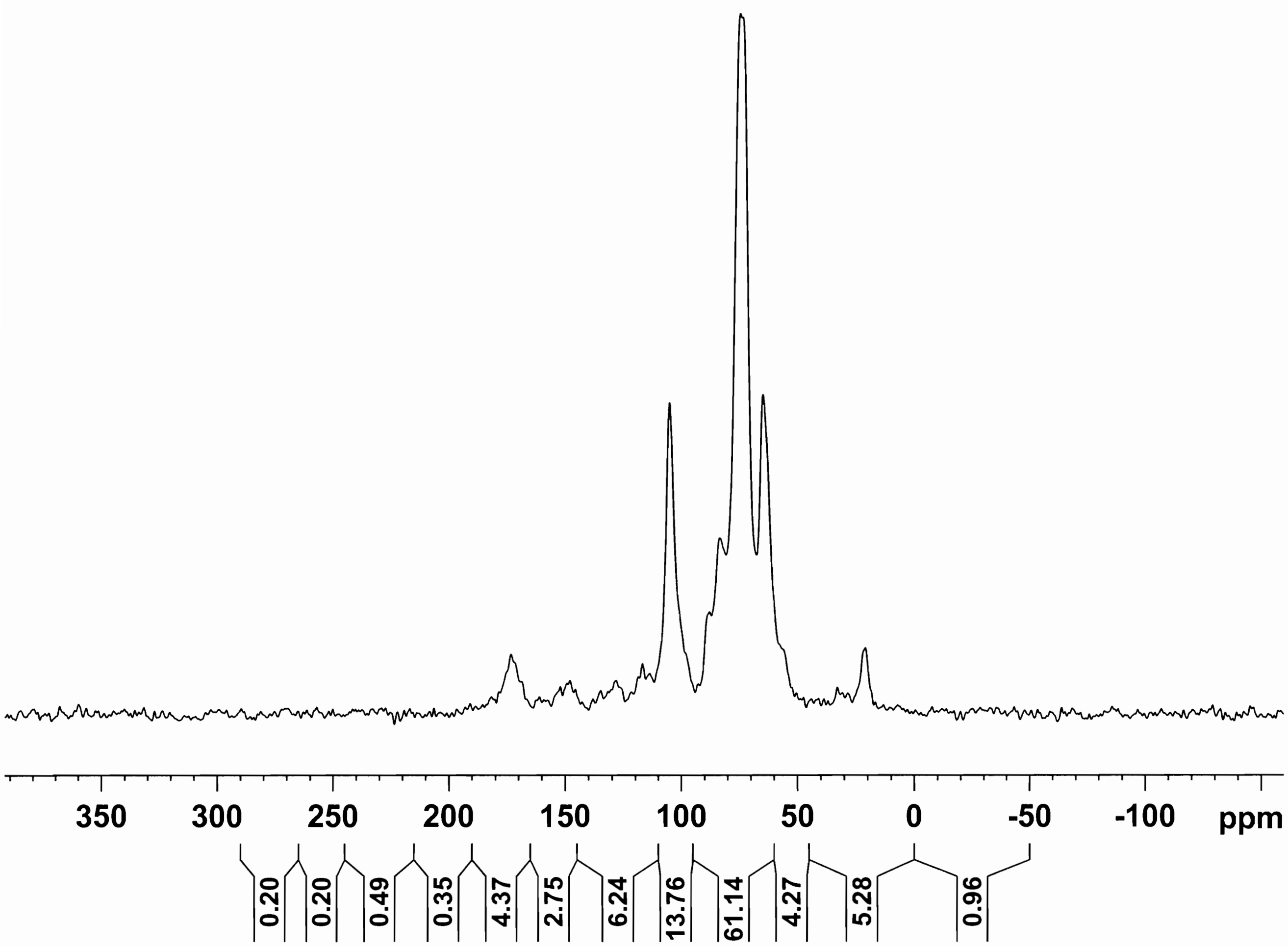
F2 - Acquisition Parameters
Date_            20080214
Time                11.19
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                 1149.4
DW                 19.800 usec
DE                   6.00 usec
TE                  697.7 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P15               1000.00 usec
PL1                  1.40 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.10 usec
P31                  5.00 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229348 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7A Rep. Support, Treatment 202 kg N/ha, Replicate 2, Cover Crop
11/28/2009 77.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC204_7A
EXPNO                  1
PROCNO                 1

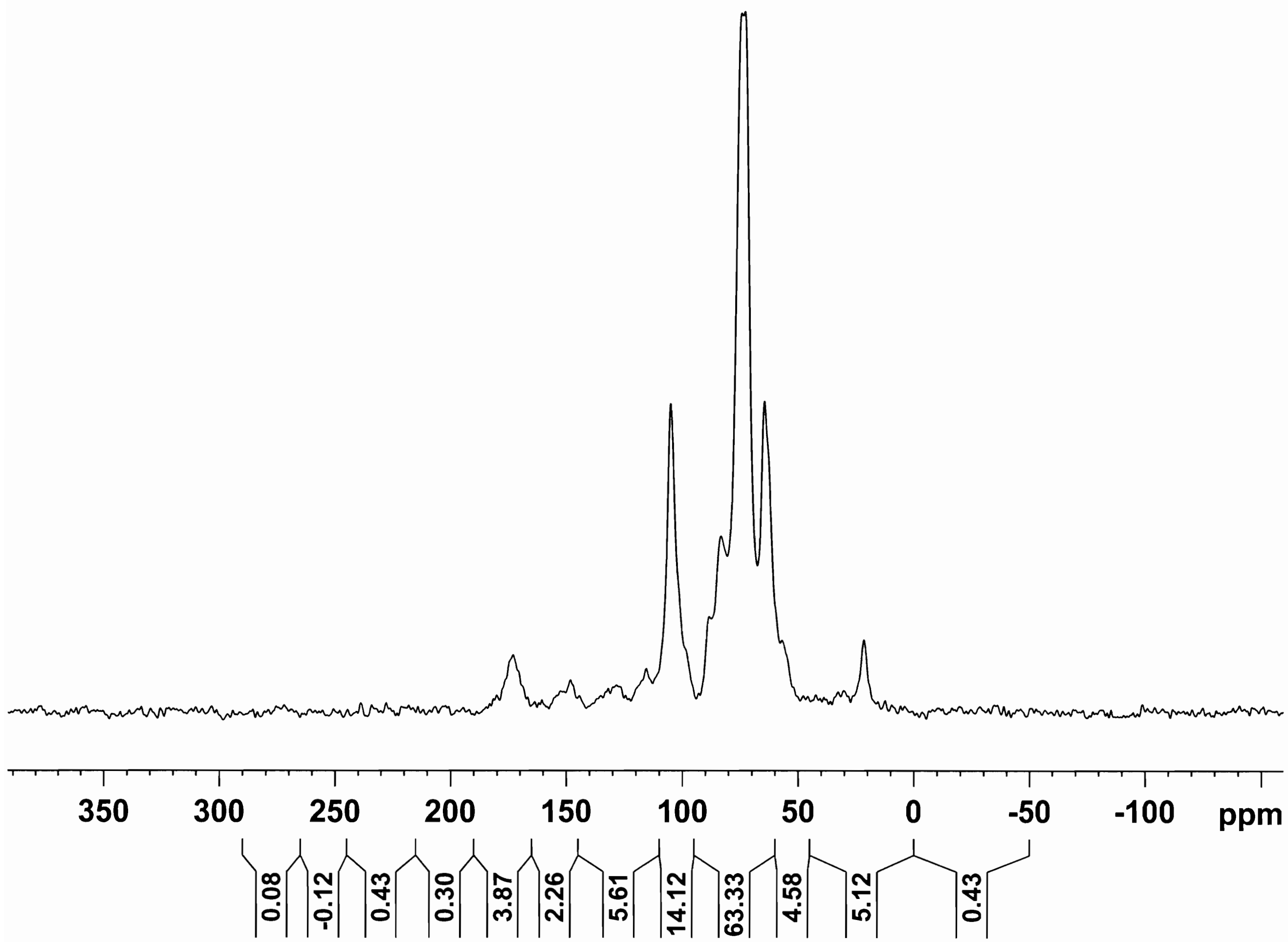
F2 - Acquisition Parameters
Date_           20091128
Time               14.50
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                  1024
SOLVENT
NS                  1000
DS                     0
SWH            27777.777 Hz
FIDRES         27.126736 Hz
AQ             0.0185000 sec
RG                  2048
DW                18.000 usec
DE                 17.00 usec
TE                 292.2 K
D1            3.00000000 sec
TD0                    4

======== CHANNEL f1 ========
NUC1                 13C
P15              1000.00 usec
PL1                 2.40 dB
SFO1          50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2           tppm15
NUC2                  1H
P3                  3.15 usec
P31                 6.00 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3228472 MHz
WDW                   EM
SSB                    0
LB                 40.00 Hz
GB                     0
PC                  1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7A Rep. Support, Treatment 202 kg N/ha, Replicate 3, Cover Crop
11/28/2009   77.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC304_7A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091128
Time	16.46
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.2 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

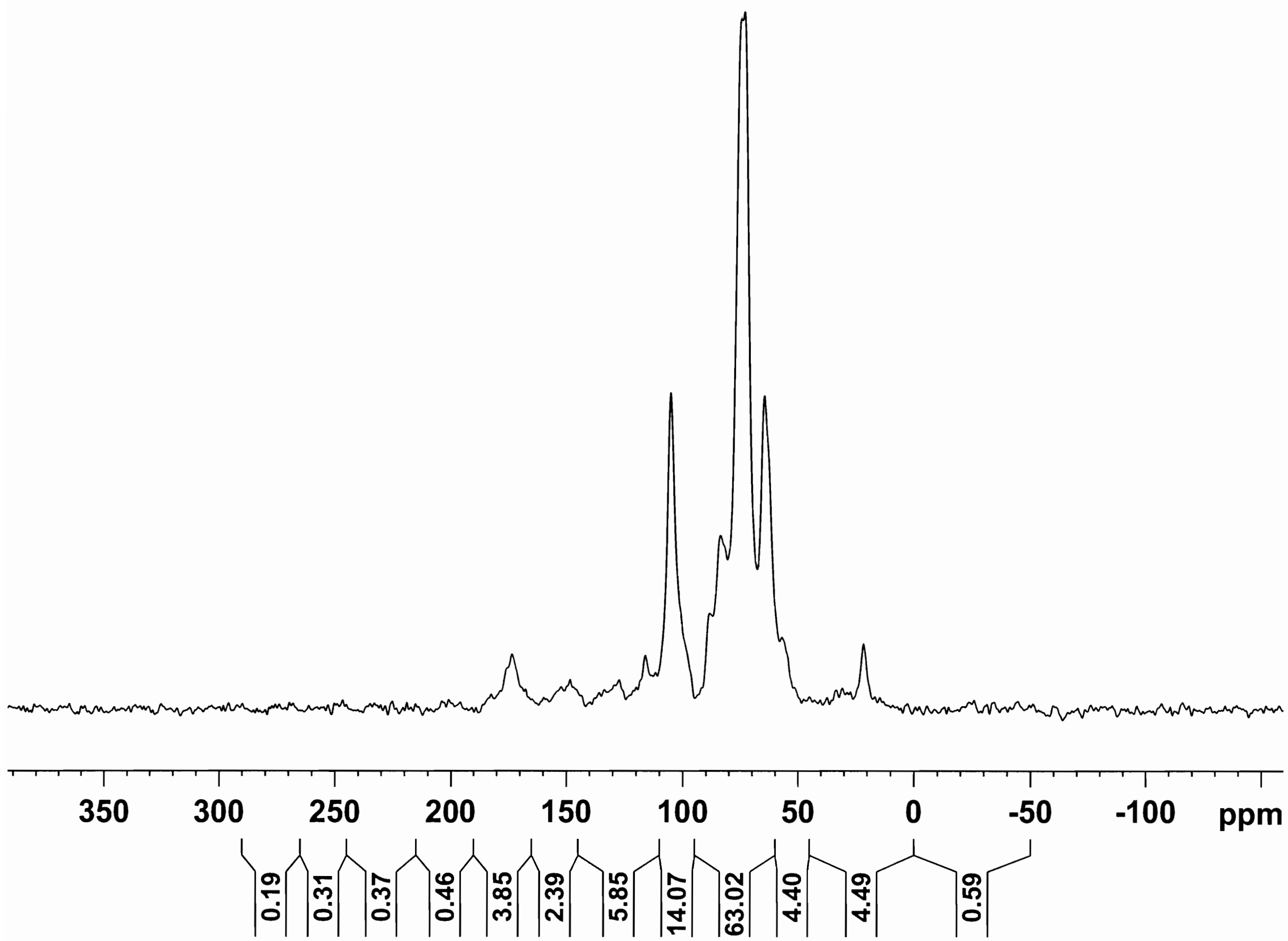
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7A Rep. Support, Treatment 202 kg N/ha, Replicate 4, Cover Crop
11/28/2009   75.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC406_7A
EXPNO                  1
PROCNO                 1

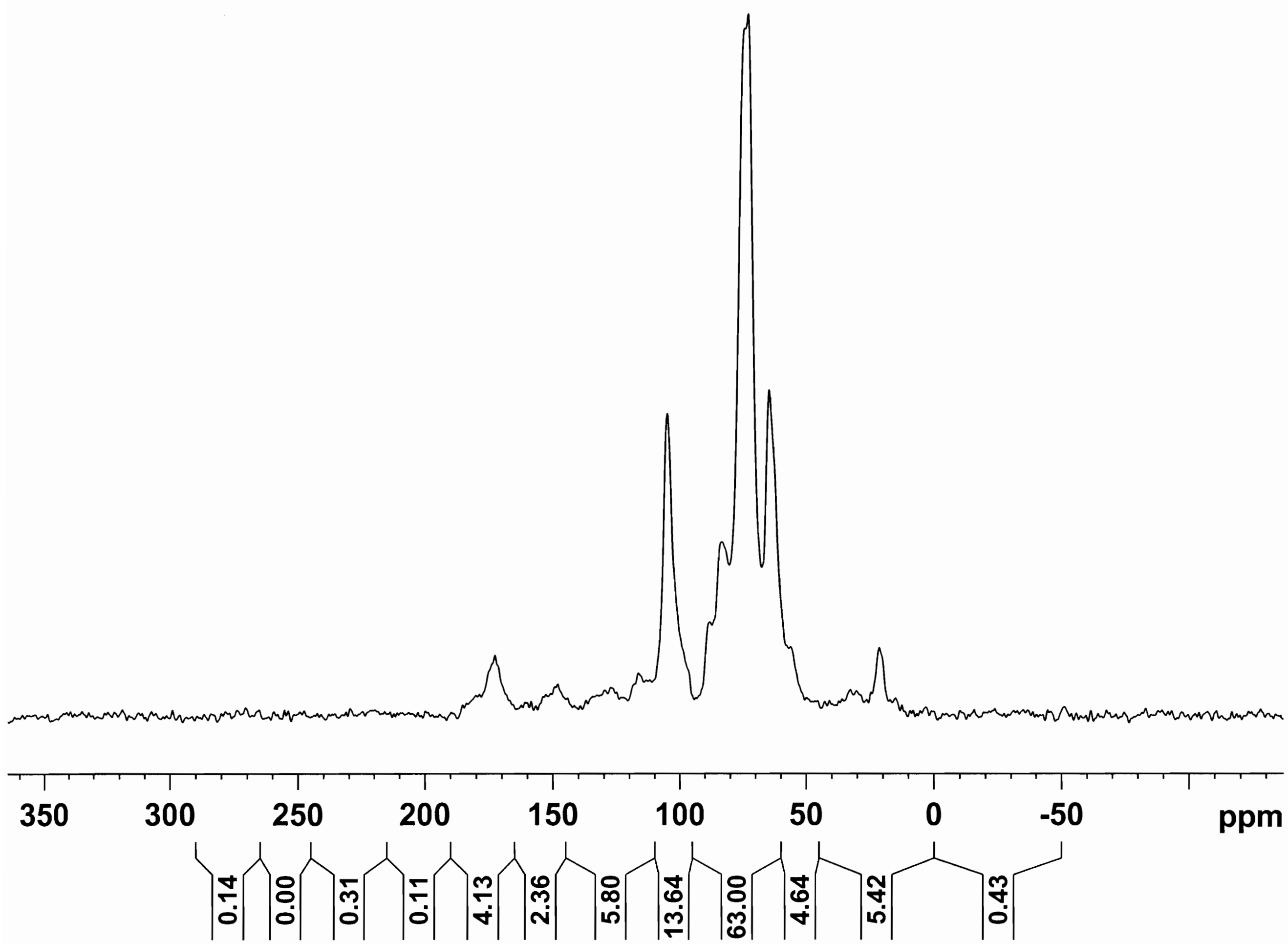
F2 - Acquisition Parameters
Date_           20091128
Time               18.46
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                  1024
SOLVENT
NS                  1000
DS                     0
SWH            27777.777 Hz
FIDRES         27.126736 Hz
AQ             0.0185000 sec
RG                  2048
DW                18.000 usec
DE                 17.00 usec
TE                 292.2 K
D1            3.00000000 sec
TD0                    4

======== CHANNEL f1 ========
NUC1                 13C
P15              1000.00 usec
PL1                 2.40 dB
SFO1          50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2           tppm15
NUC2                  1H
P3                  3.15 usec
P31                 6.00 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3228472 MHz
WDW                   EM
SSB                    0
LB                 40.00 Hz
GB                     0
PC                  1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Rep. Support, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/13/2008   67.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC101_1B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080313
Time	13.46
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	1625.5
DW	19.800 usec
DE	6.00 usec
TE	698.0 K
D1	2.00000000 sec

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz

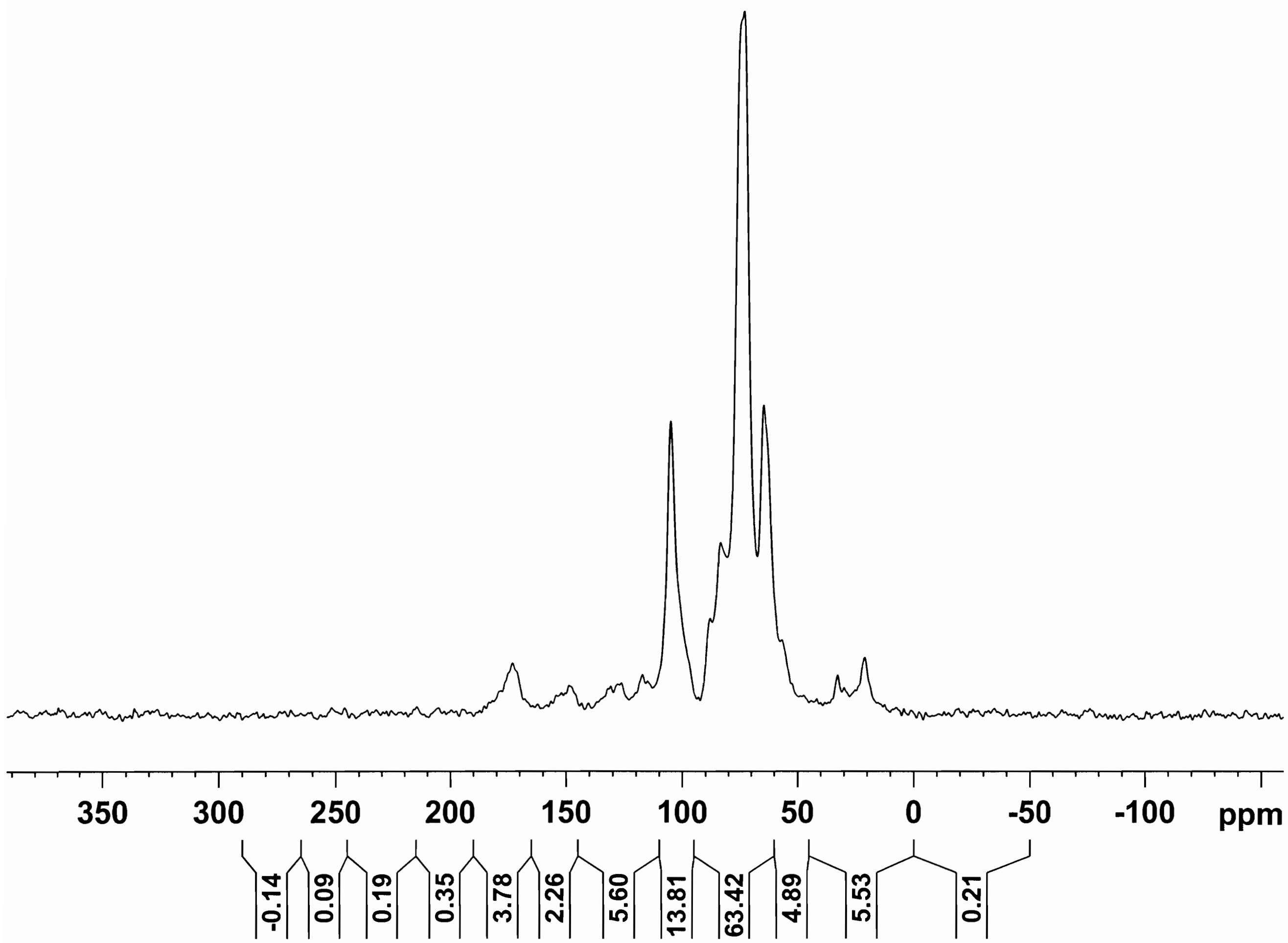
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229662 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 203_1B Rep. Support, Treatment 0 kg N/ha, Replicate 2, No Cover Crop
11/11/2009 69.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC203_1B
EXPNO                     1
PROCNO                    1

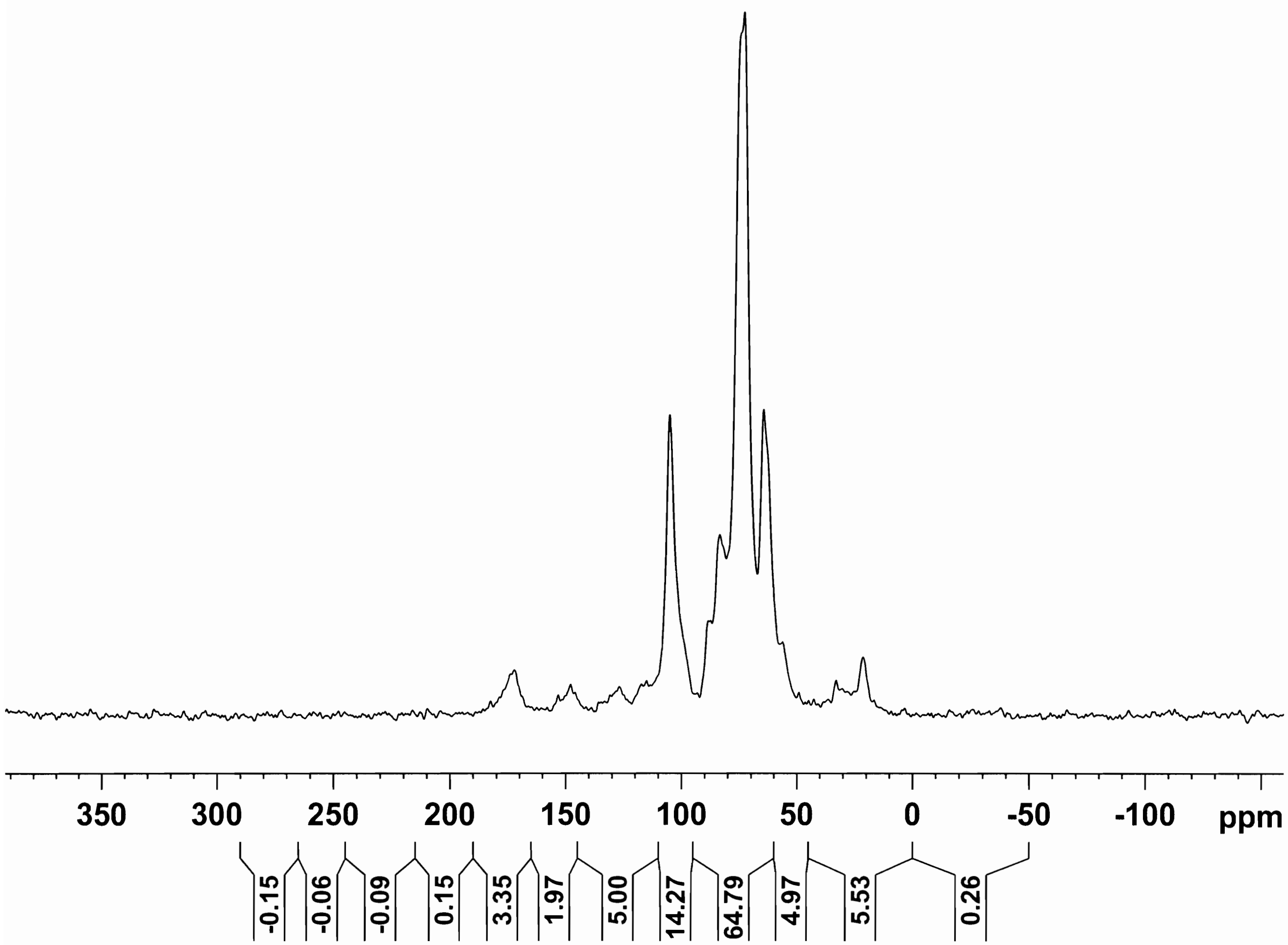
F2 - Acquisition Parameters
Date_              20091111
Time                  20.11
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                     1024
SOLVENT
NS                     2000
DS                        0
SWH               27777.777 Hz
FIDRES            27.126736 Hz
AQ                0.0185000 sec
RG                     2048
DW                   18.000 usec
DE                    17.00 usec
TE                    292.5 K
D1               3.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                    13C
P15                 1000.00 usec
PL1                    2.40 dB
SFO1             50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.15 usec
P31                    6.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3228472 MHz
WDW                      EM
SSB                       0
LB                    40.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 307_1B Rep. Support, Treatment 0 kg N/ha, Replicate 3, No Cover Crop
11/12/2009 72.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC307_1B
EXPNO                      1
PROCNO                     1

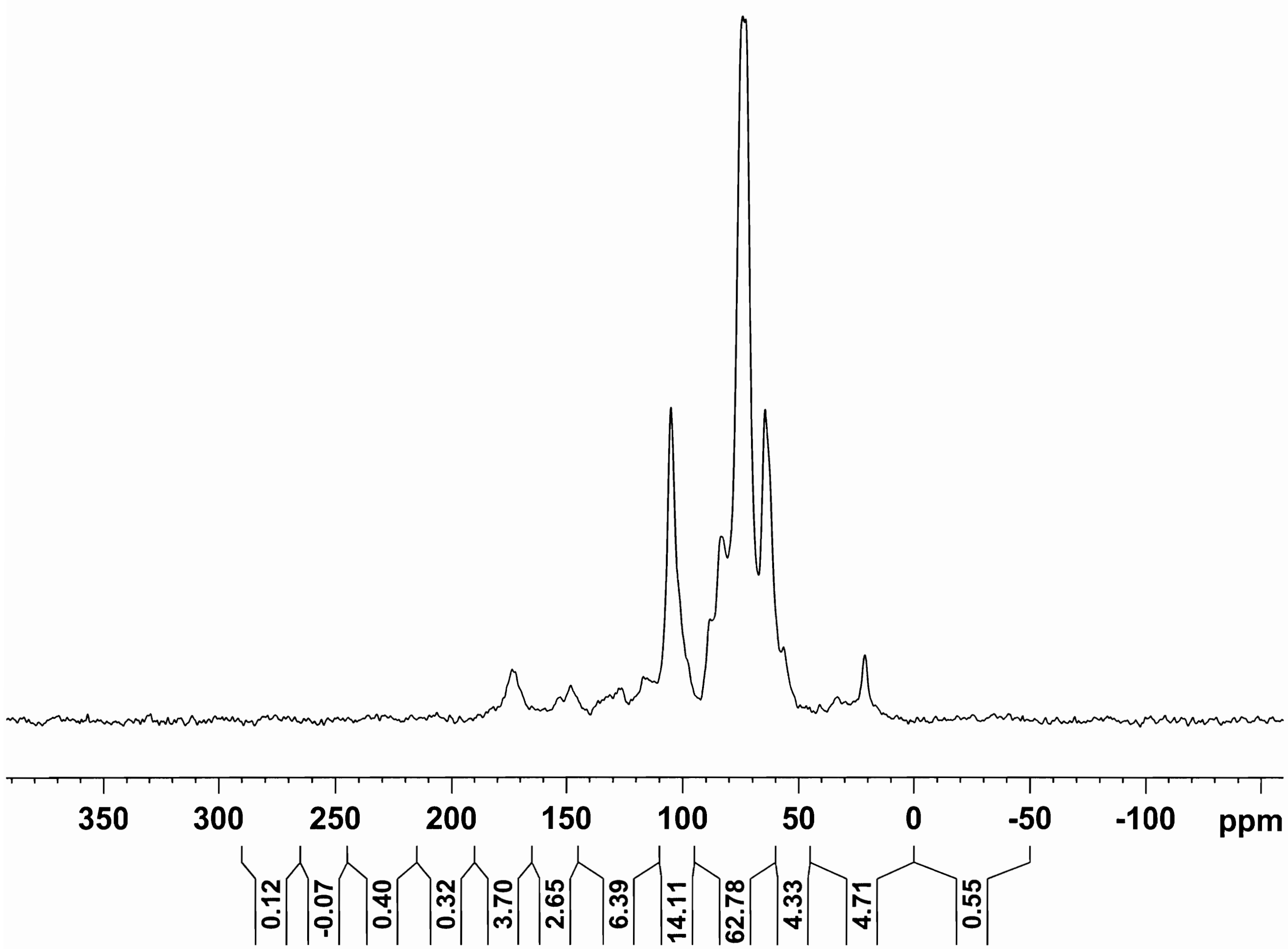
F2 - Acquisition Parameters
Date_             20091112
Time                 21.26
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                    1024
SOLVENT
NS                    2000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   293.0 K
D1              3.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 402_1B Rep. Support, Treatment 0 kg N/ha, Replicate 4, No Cover Crop
11/12/2009   74.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



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Current Data Parameters

NAME	KBSNRate_HSTC402_1B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20091112
Time	11.18
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	2000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	293.2 K
D1	3.00000000 sec
TD0	8

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

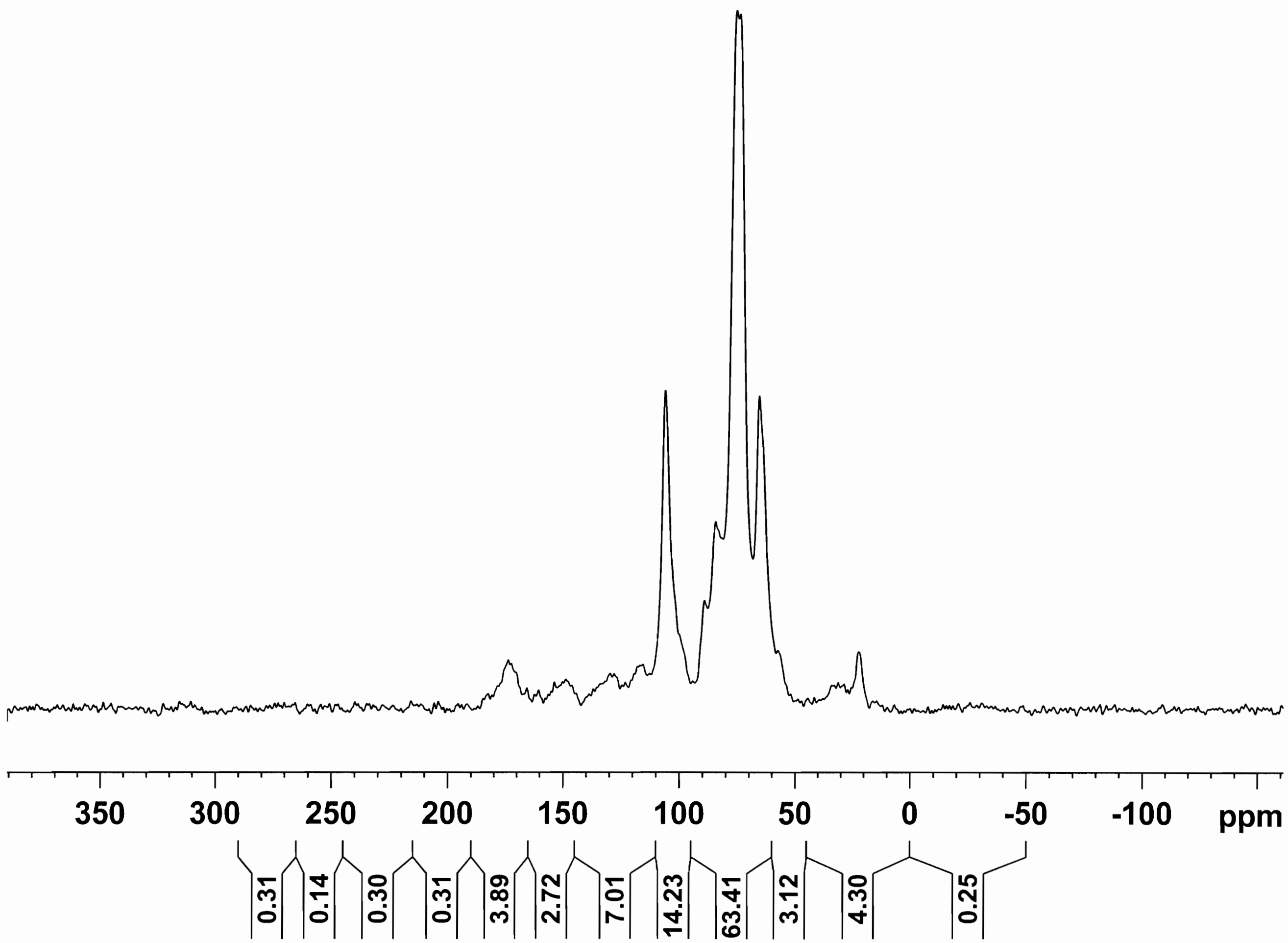
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Rep. Support, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
07/16/2008   62.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME   KBSNRate_HSTC107_2B
EXPNO   1
PROCNO   1

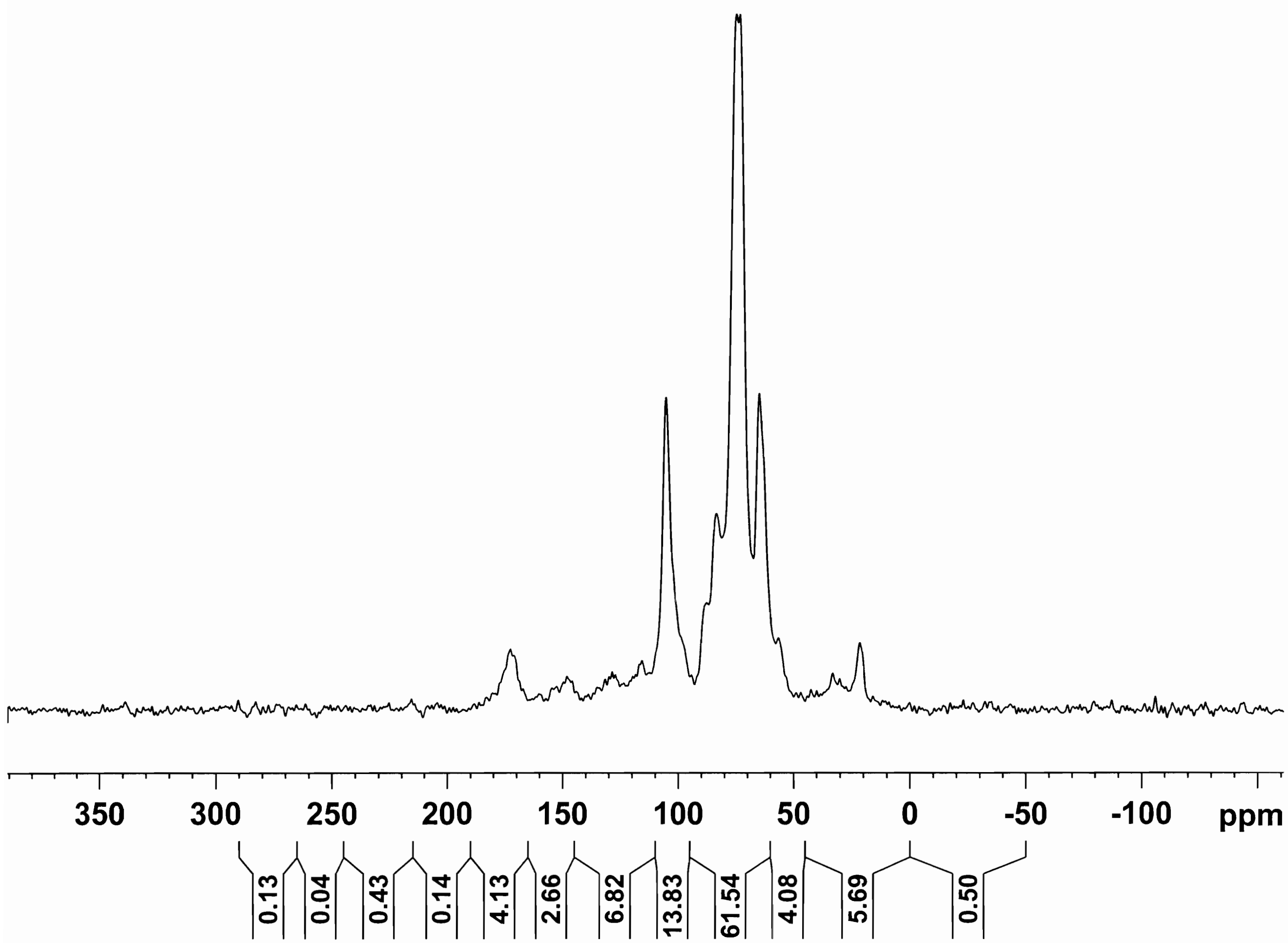
F2 - Acquisition Parameters
Date_   20080717
Time   0.10
INSTRUM spect
PROBHD   4 mm MASxvt BB
PULPROG cp.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2048
DW   18.000 usec
DE   6.00 usec
TE   697.7 K
D1   2.00000000 sec

======== CHANNEL f1 ========
NUC1   13C
P15   1000.00 usec
PL1   1.40 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2   1H
P3   3.15 usec
P31   5.80 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229317 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Rep. Support, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
07/17/2008   61.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC106_3B
EXPNO                  1
PROCNO                 1

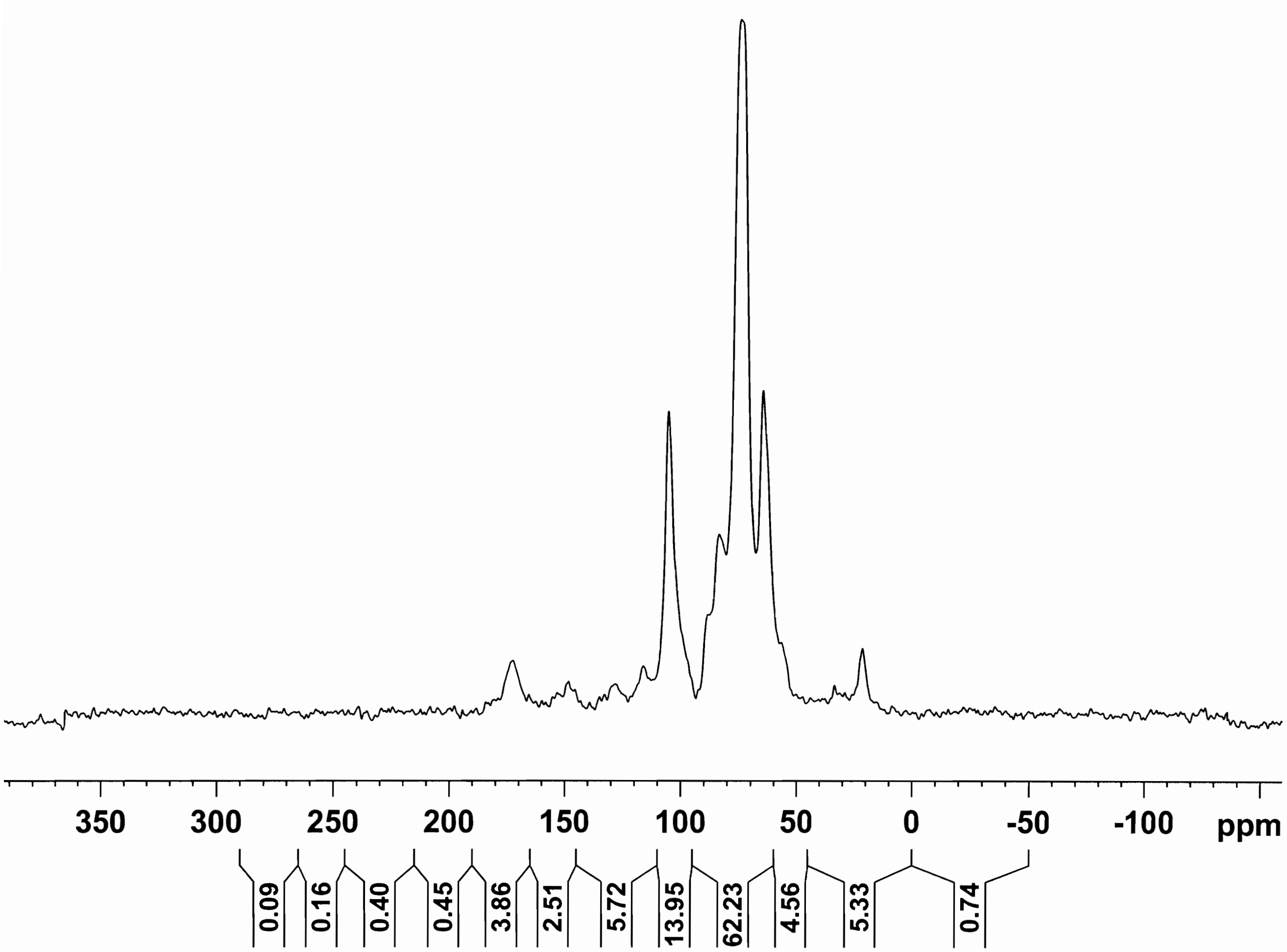
F2 - Acquisition Parameters
Date_          20080717
Time              14.59
INSTRUM           spect
PROBHD   4 mm MASxvt BB
PULPROG       cp.99.LBA
TD                 1024
SOLVENT
NS                 3500
DS                    0
SWH           27777.777 Hz
FIDRES        27.126736 Hz
AQ            0.0185000 sec
RG                 2048
DW               18.000 usec
DE                 6.00 usec
TE                698.0 K
D1           2.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P15             1000.00 usec
PL1                1.40 dB
SFO1         50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2          tppm15
NUC2                 1H
P3                 3.15 usec
P31                5.80 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                16384
SF           50.3229317 MHz
WDW                  EM
SSB                   0
LB                30.00 Hz
GB                    0
PC                 1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 202_3B Rep. Support, Treatment 67 kg N/ha, Replicate 2, No Cover Crop
11/14/2009   68.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC202_3B
EXPNO                      1
PROCNO                     1

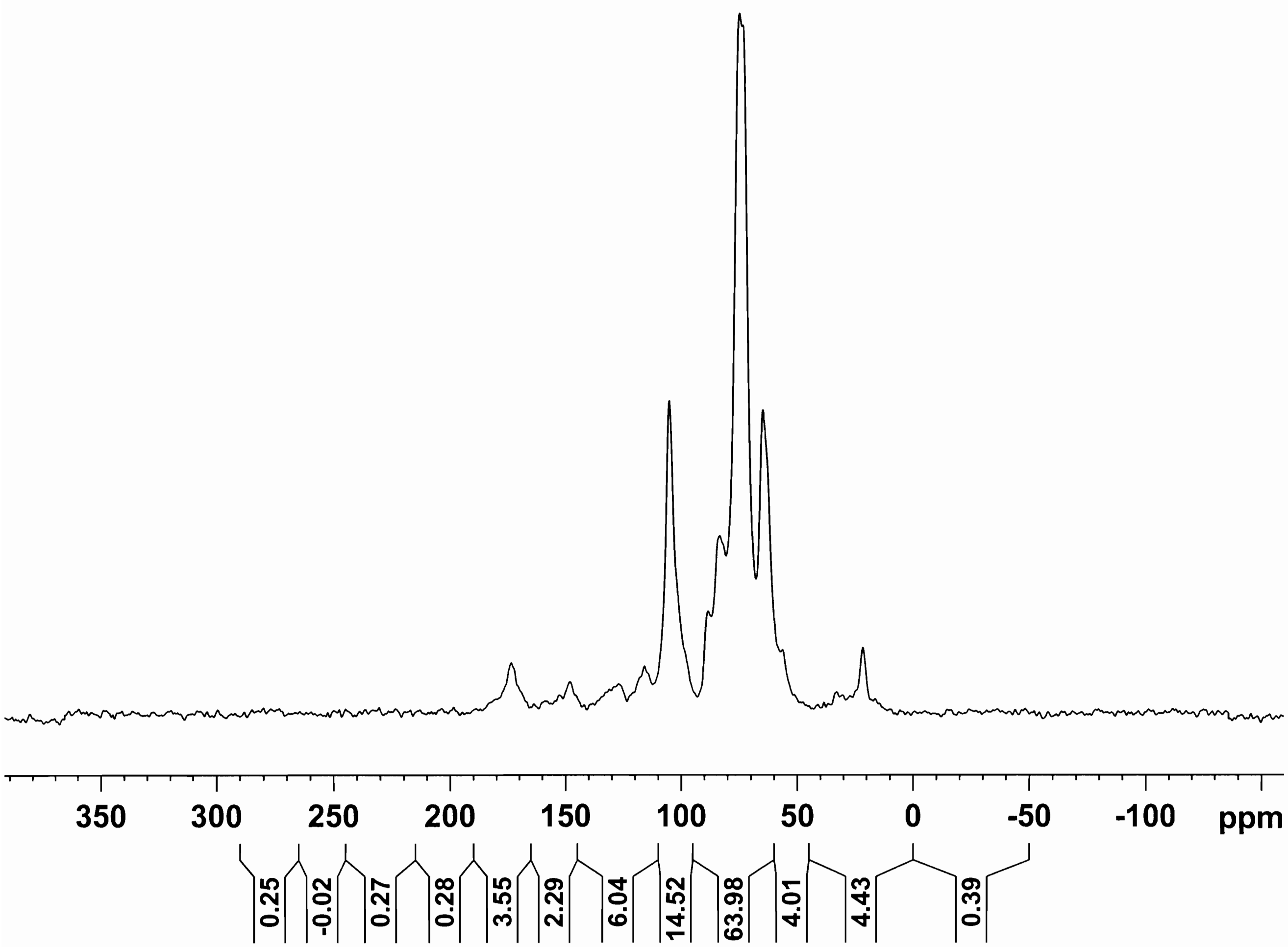
F2 - Acquisition Parameters
Date_             20091114
Time                 14.59
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    1701
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   293.1 K
D1              3.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 305_3B Rep. Support, Treatment 67 kg N/ha, Replicate 3, No Cover Crop
11/14/2009   80.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC305_3B
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20091114
Time                  21.25
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                     1024
SOLVENT
NS                     2000
DS                        0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                     2048
DW                   18.000 usec
DE                    17.00 usec
TE                    292.4 K
D1               3.00000000 sec
TD0                       8

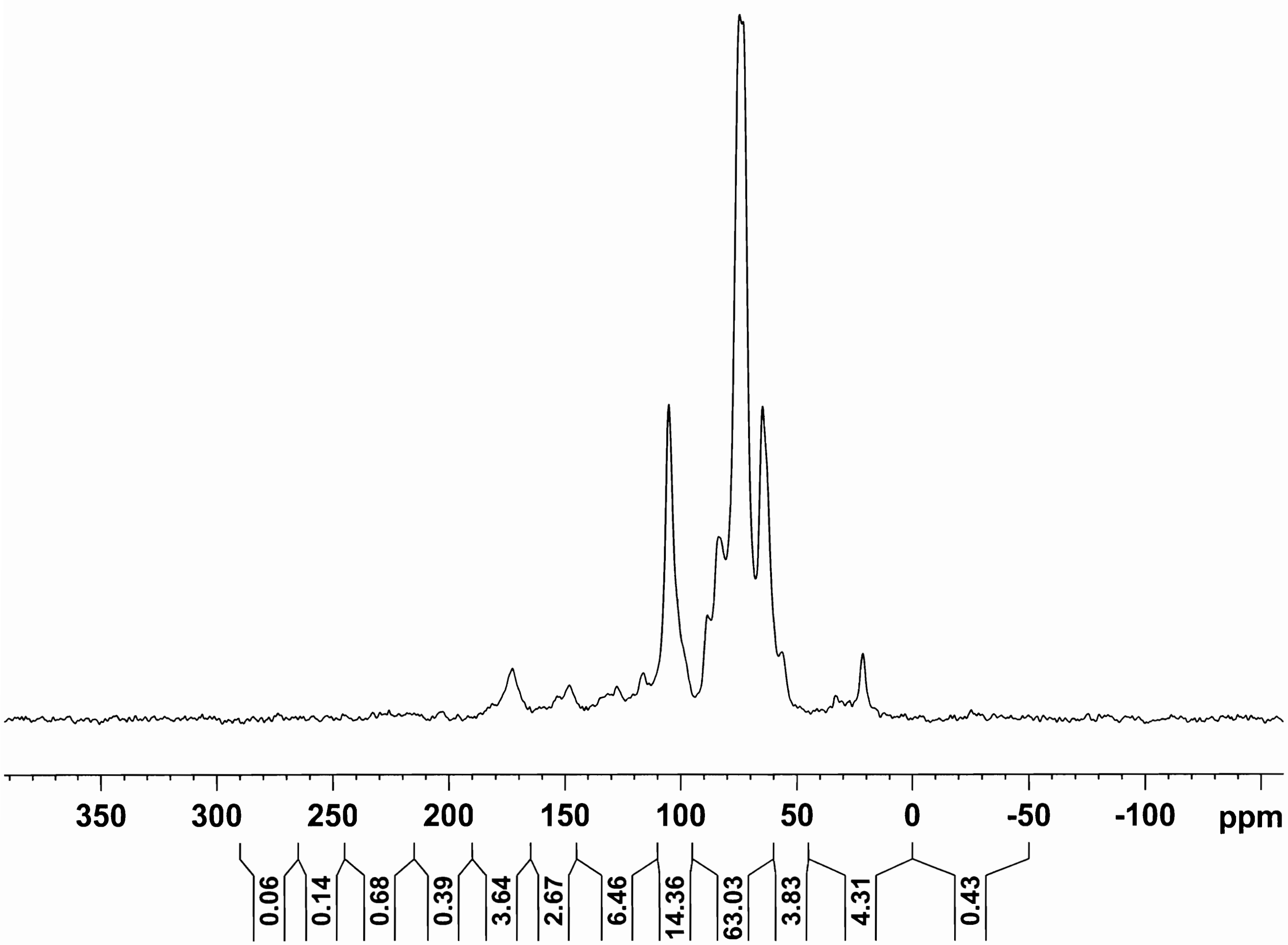
======== CHANNEL f1 ========
NUC1                    13C
P15                 1000.00 usec
PL1                    2.40 dB
SFO1             50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.15 usec
P31                    6.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3228472 MHz
WDW                      EM
SSB                       0
LB                    40.00 Hz
GB                        0
PC                     1.00
```

393

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 404_3B Rep. Support, Treatment 67 kg N/ha, Replicate 4, No Cover Crop
11/15/2009   82.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_HSTC404_3B
EXPNO 1
PROCNO 1

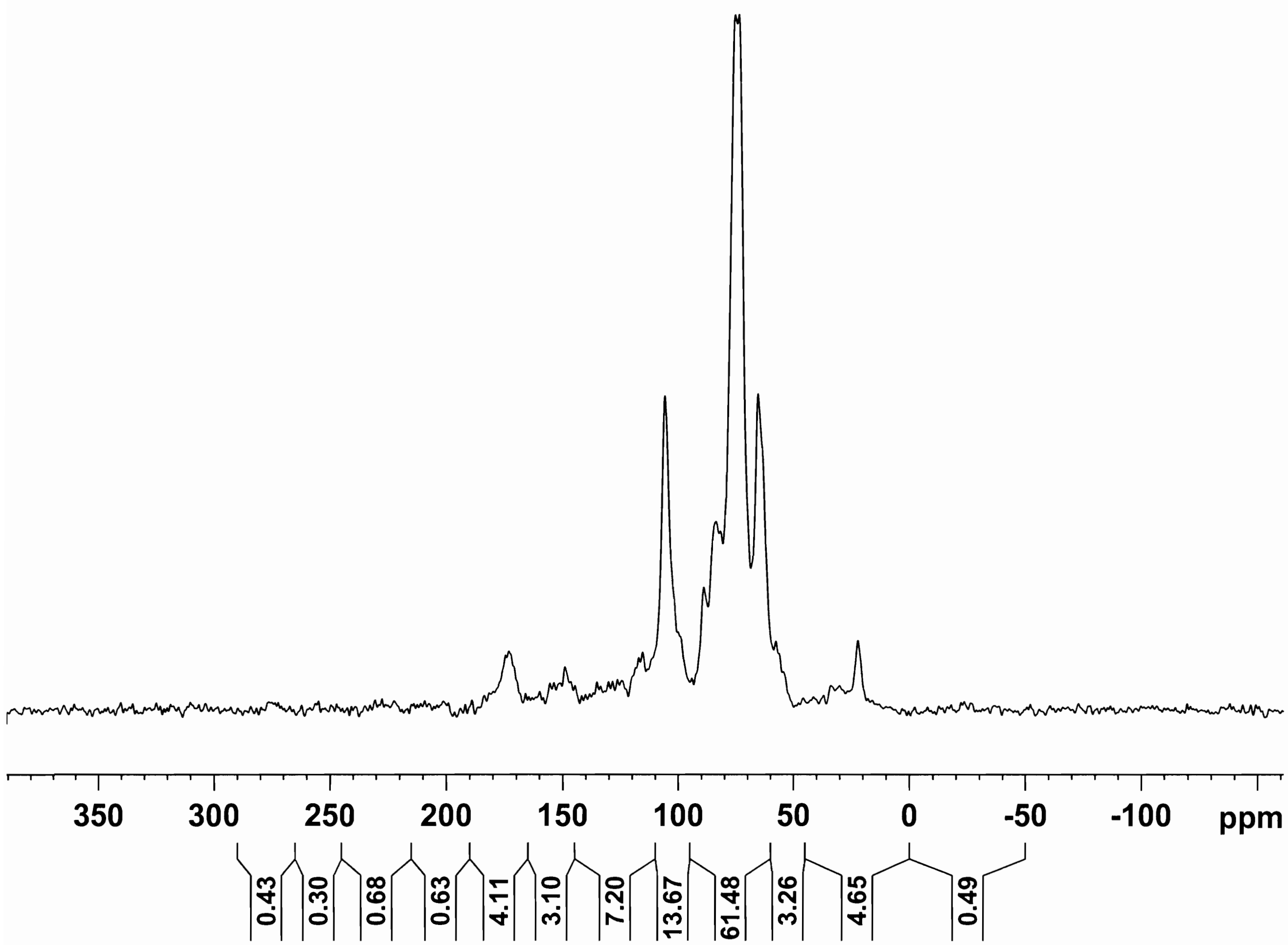
F2 - Acquisition Parameters
Date_ 20091115
Time 13.49
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 2000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.4 K
D1 3.00000000 sec
TD0 8

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Rep. Support, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
07/16/2008   63.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC102_4B
EXPNO                   1
PROCNO                  1

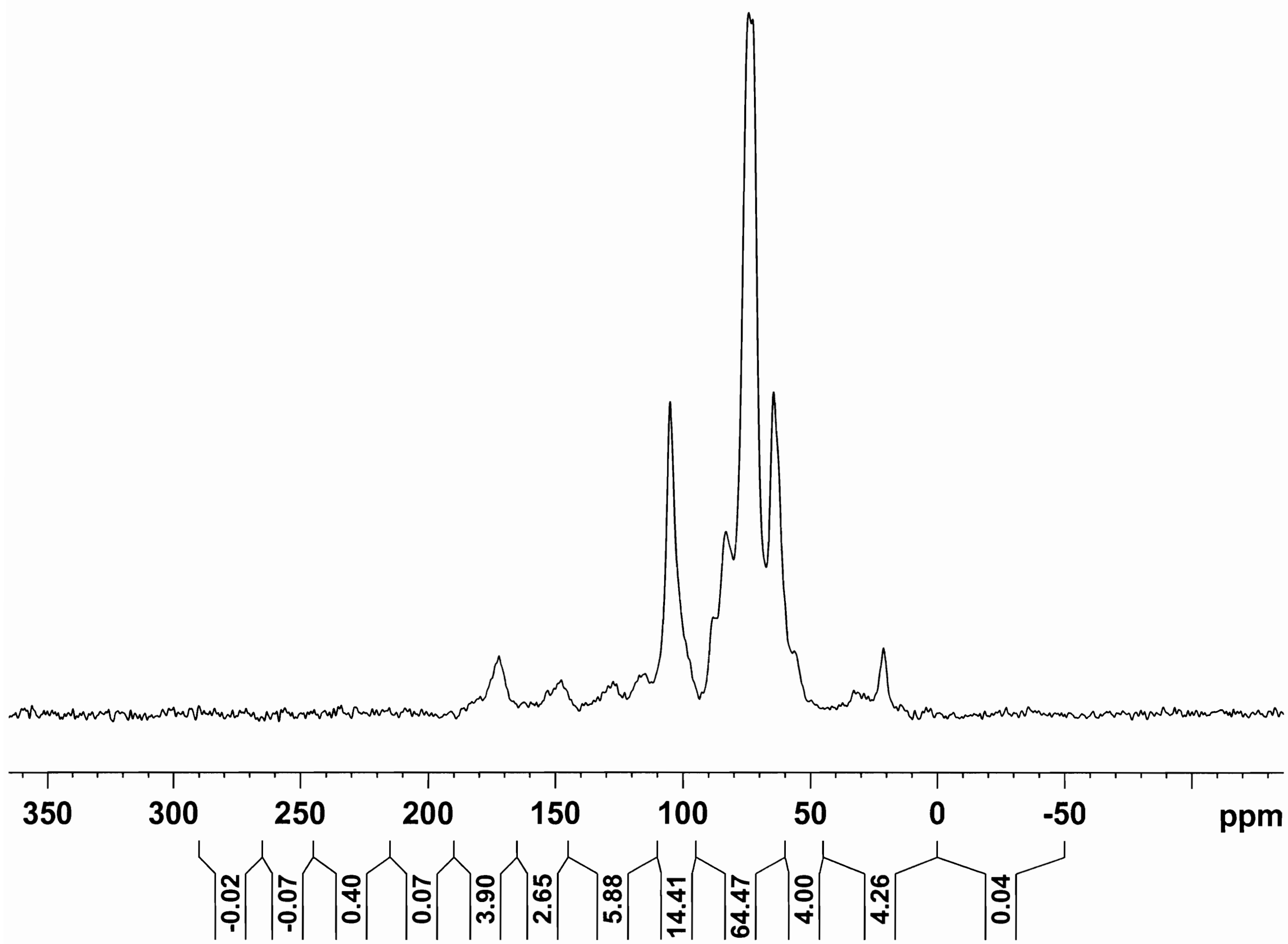
F2 - Acquisition Parameters
Date_          20080716
Time              19.20
INSTRUM           spect
PROBHD   4 mm MASxvt BB
PULPROG       cp.99.LBA
TD                 1024
SOLVENT
NS                 3500
DS                    0
SWH           27777.777 Hz
FIDRES        27.126736 Hz
AQ            0.0185000 sec
RG                 2048
DW               18.000 usec
DE                 6.00 usec
TE                697.9 K
D1           2.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P15             1000.00 usec
PL1                1.40 dB
SFO1         50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2          tppm15
NUC2                 1H
P3                 3.15 usec
P31                5.80 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                16384
SF           50.3229317 MHz
WDW                  EM
SSB                   0
LB                30.00 Hz
GB                    0
PC                 1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Rep. Support, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/30/2008   65.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters

NAME	KBSNRate_HSTC104_5B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20080630
Time	13.55
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2048
DW	19.800 usec
DE	6.00 usec
TE	696.8 K
D1	2.00000000 sec

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	1.40 dB
SFO1	50.3287071 MHz

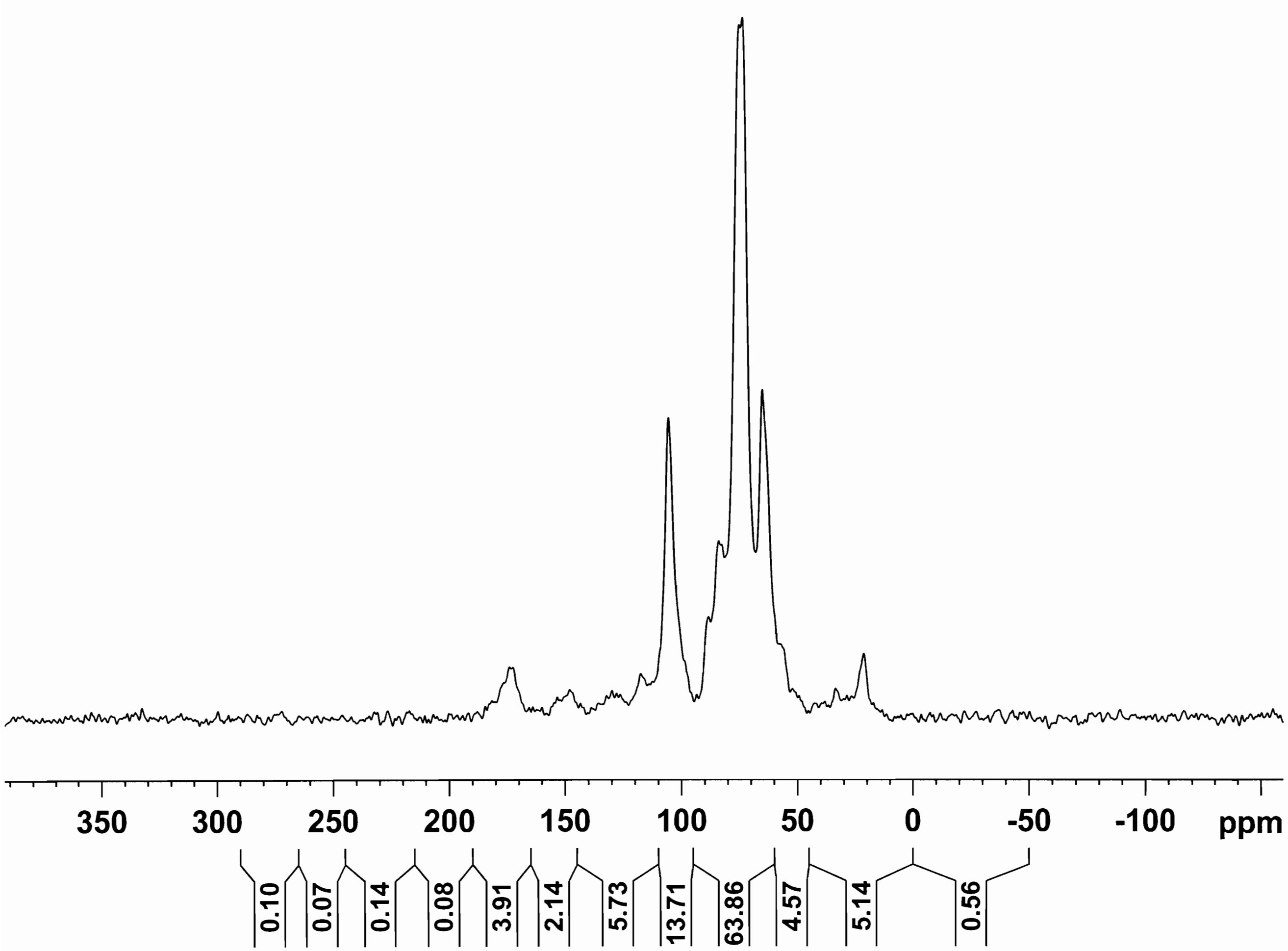
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.20 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229333 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 205_5B Rep. Support, Treatment 134 kg N/ha, Replicate 2, No Cover Crop
12/31/2009   71.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_HSTC205_5B
EXPNO                   1
PROCNO                  1

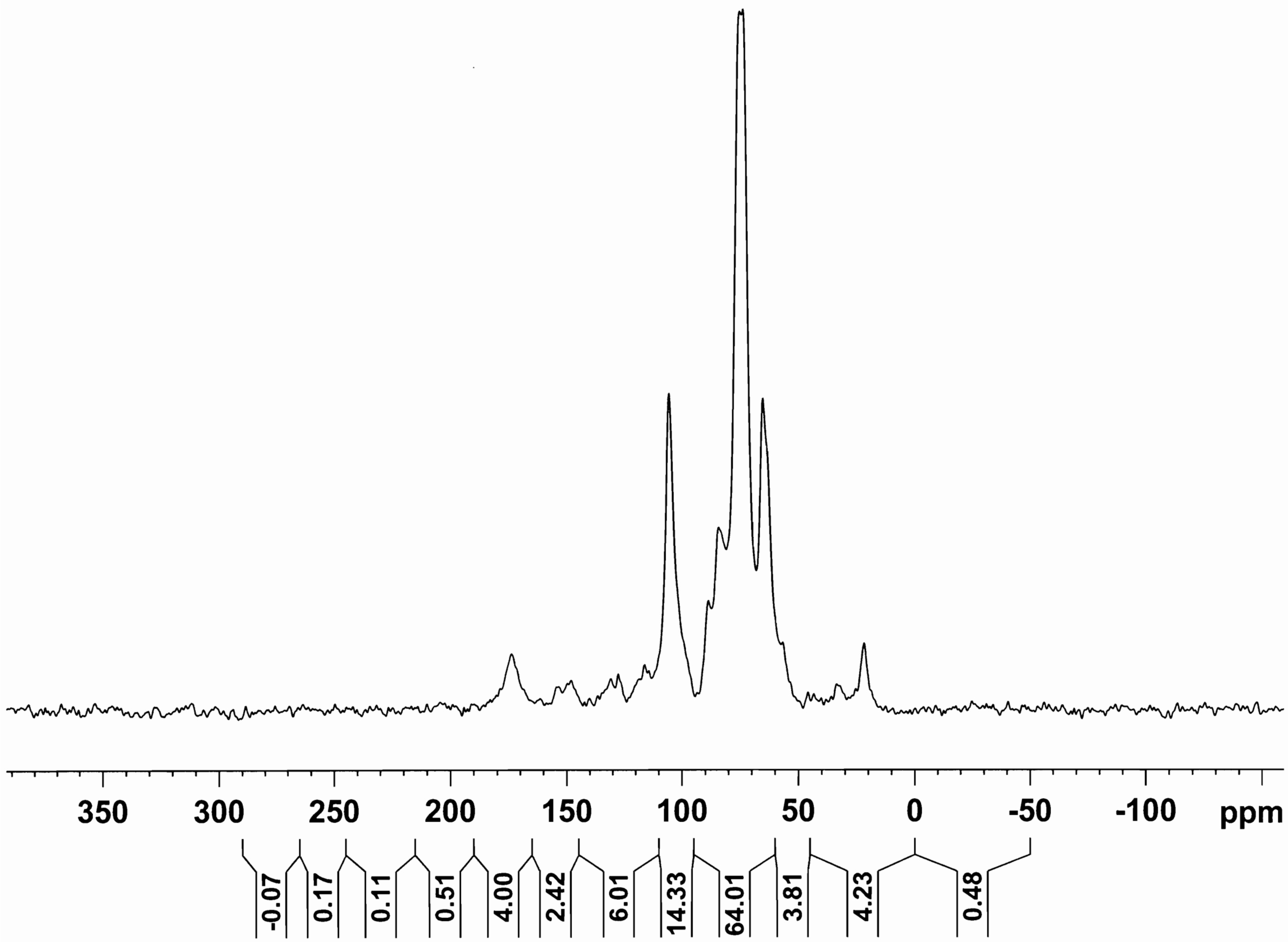
F2 - Acquisition Parameters
Date_            20091231
Time                14.53
INSTRUM             spect
PROBHD    4 mm MASxvt BB
PULPROG        cp.99.WCH
TD                   1024
SOLVENT
NS                   1000
DS                      0
SWH           27777.777 Hz
FIDRES        27.126736 Hz
AQ            0.0185000 sec
RG                   2048
DW               18.000 usec
DE                17.00 usec
TE                292.1 K
D1           3.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  13C
P15             1000.00 usec
PL1                2.40 dB
SFO1         50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                 3.15 usec
P31                6.00 usec
PL2                6.00 dB
PL12               3.00 dB
SFO2        200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF           50.3228472 MHz
WDW                    EM
SSB                     0
LB                40.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 302_5B Rep. Support, Treatment 134 kg N/ha, Replicate 3, No Cover Crop
01/02/2010   74.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_HSTC302_5B
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100102
Time 15.24
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 1000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.2 K
D1 3.00000000 sec
TD0 4

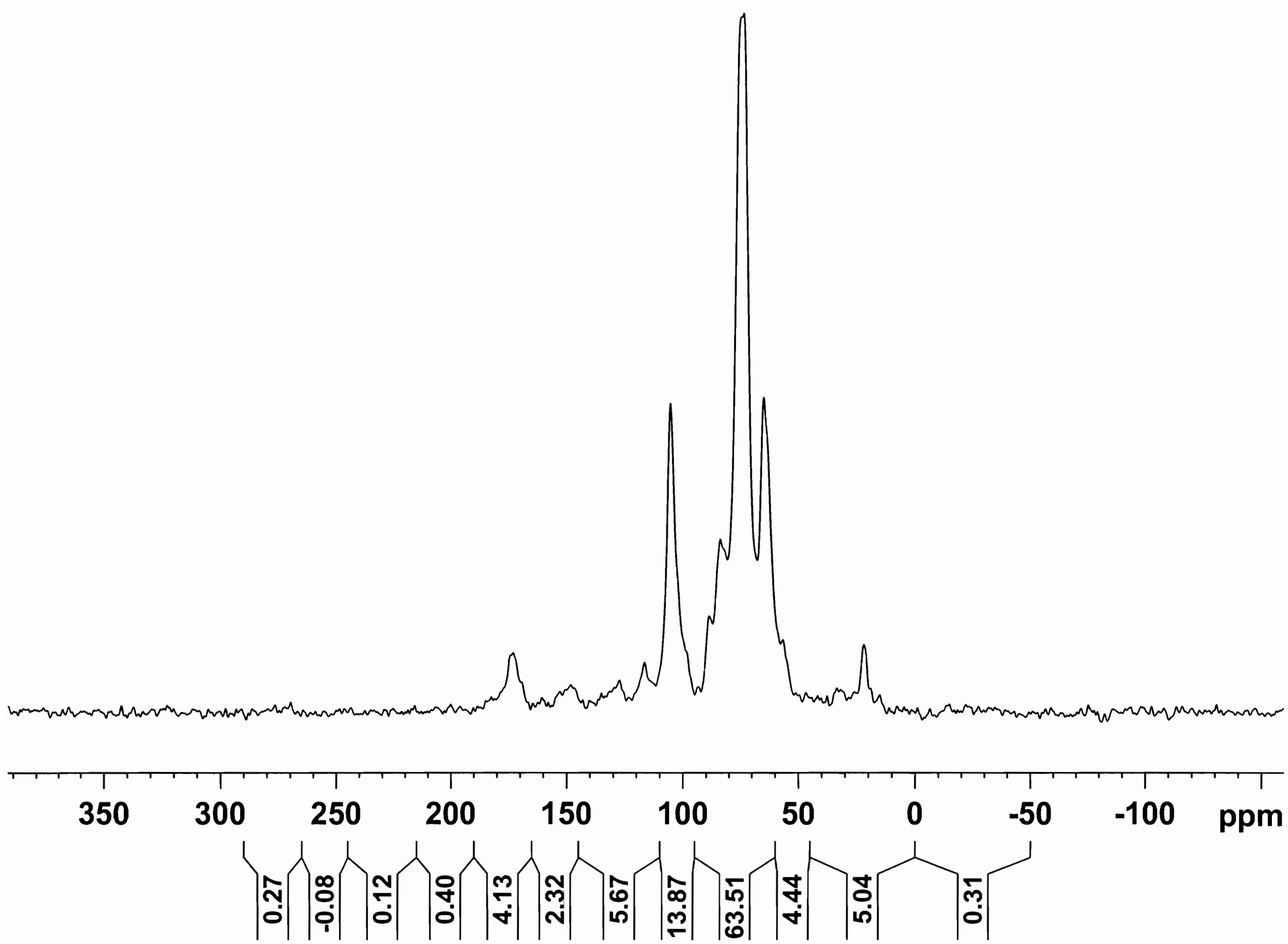
======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 407_5B Rep. Support, Treatment 134 kg N/ha, Replicate 4, No Cover Crop
01/02/2010   72.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.

BRUKER



Current Data Parameters

NAME	KBSNRate_HSTC407_5B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20100102
Time	16.22
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cp.99.WCH
TD	1024
SOLVENT	
NS	1000
DS	0
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2048
DW	18.000 usec
DE	17.00 usec
TE	292.2 K
D1	3.00000000 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P15	1000.00 usec
PL1	2.40 dB
SFO1	50.3287070 MHz

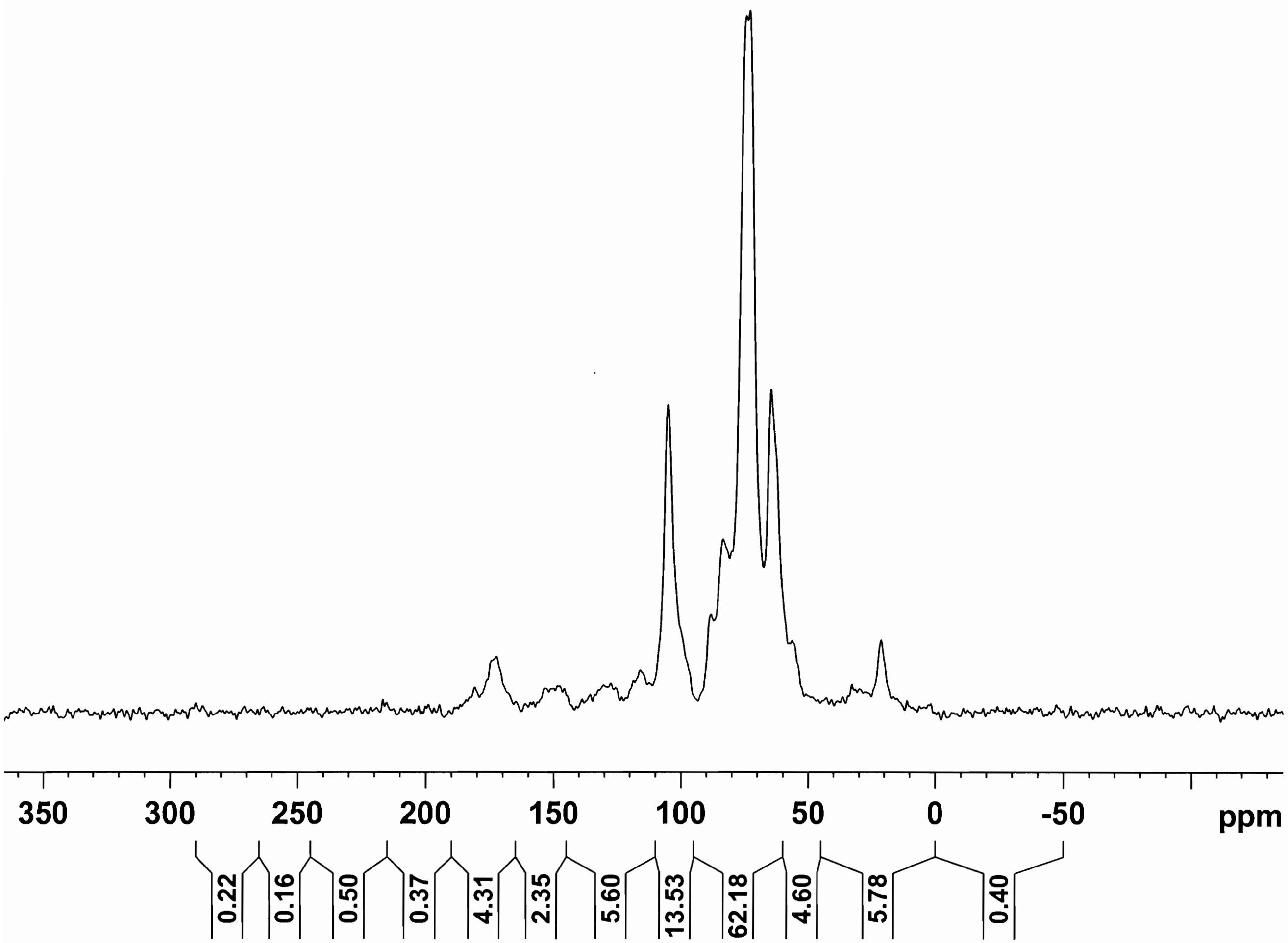
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.15 usec
P31	6.00 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3228472 MHz
WDW	EM
SSB	0
LB	40.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Rep. Support, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/30/2008   62.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



BRUKER

Current Data Parameters
NAME KBSNRate_HSTC103_6B
EXPNO 1
PROCNO 1

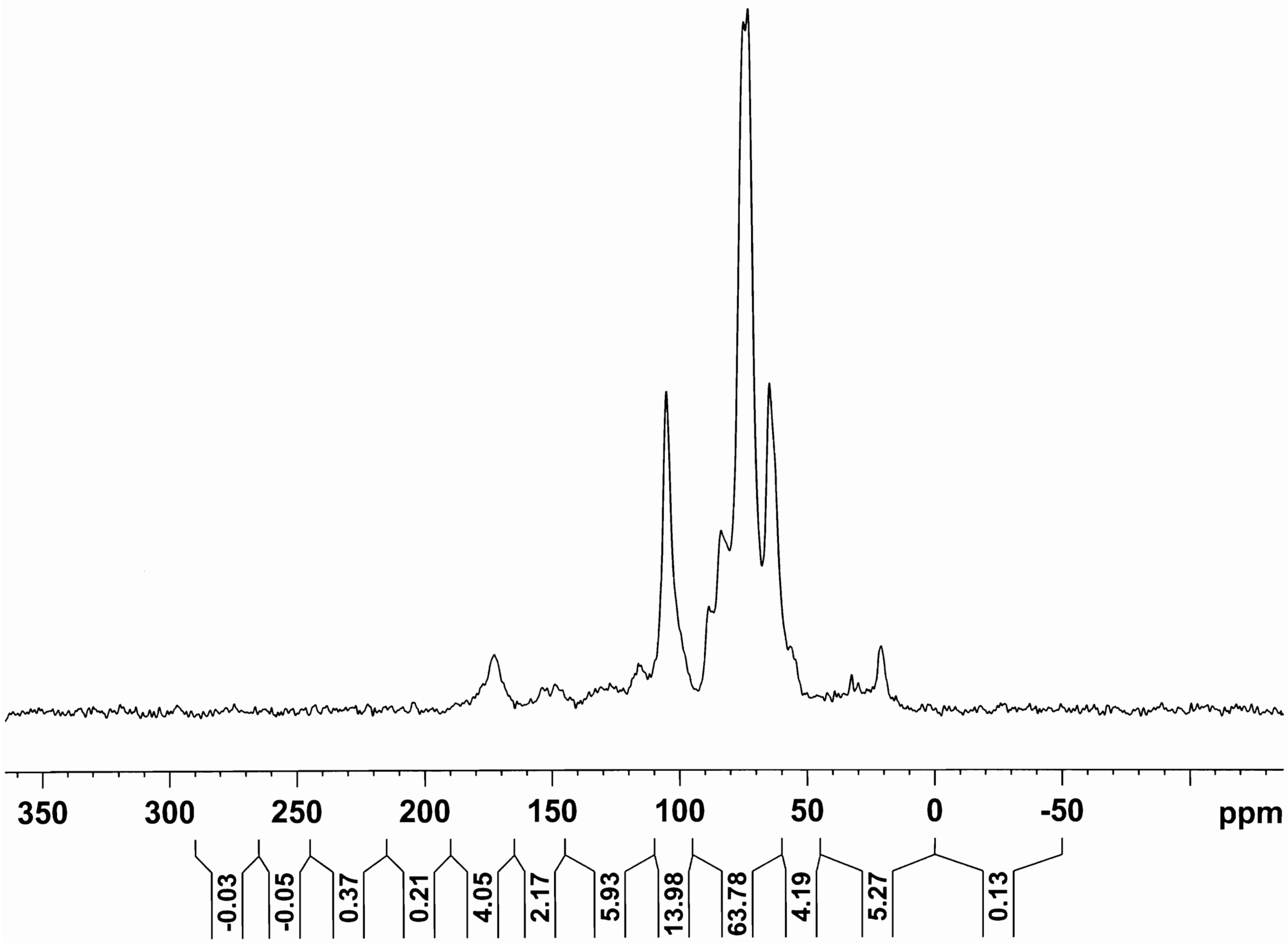
F2 - Acquisition Parameters
Date_ 20080630
Time 18.38
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2048
DW 19.800 usec
DE 6.00 usec
TE 697.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 1.40 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.20 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229333 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Rep. Support, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/13/2008 56.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME      KBSNRate_HSTC105_7B
EXPNO                       1
PROCNO                      1

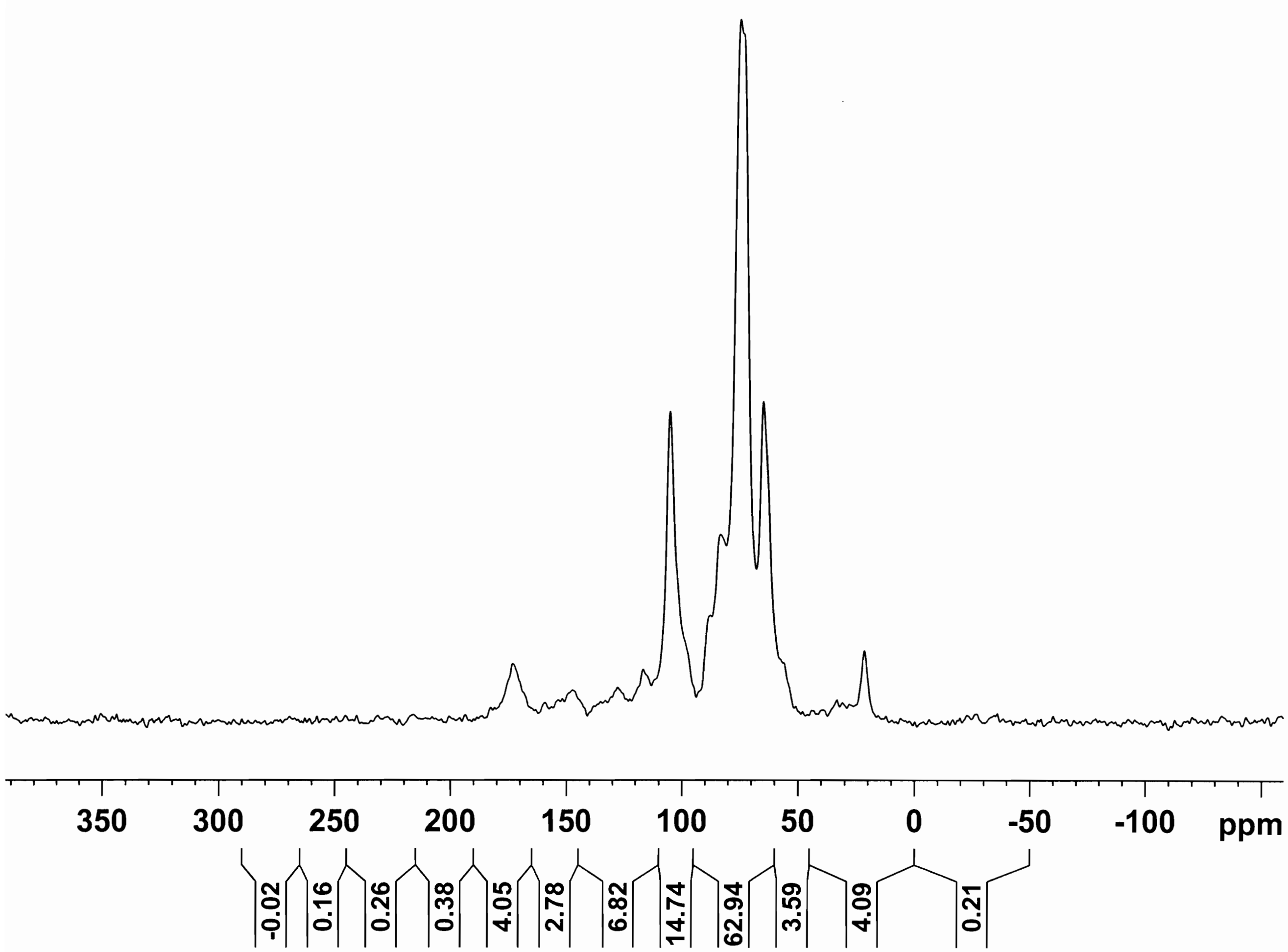
F2 - Acquisition Parameters
Date_            20080313
Time                16.39
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                1149.4
DW                19.800 usec
DE                  6.00 usec
TE                 698.0 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P15              1000.00 usec
PL1                 1.40 dB
SFO1          50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                  3.05 usec
P31                 5.10 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229662 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 204_7B Rep. Support, Treatment 202 kg N/ha, Replicate 2, No Cover Crop
11/11/2009   76.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.



Current Data Parameters
NAME KBSNRate_HSTC204_7B
EXPNO 1
PROCNO 1

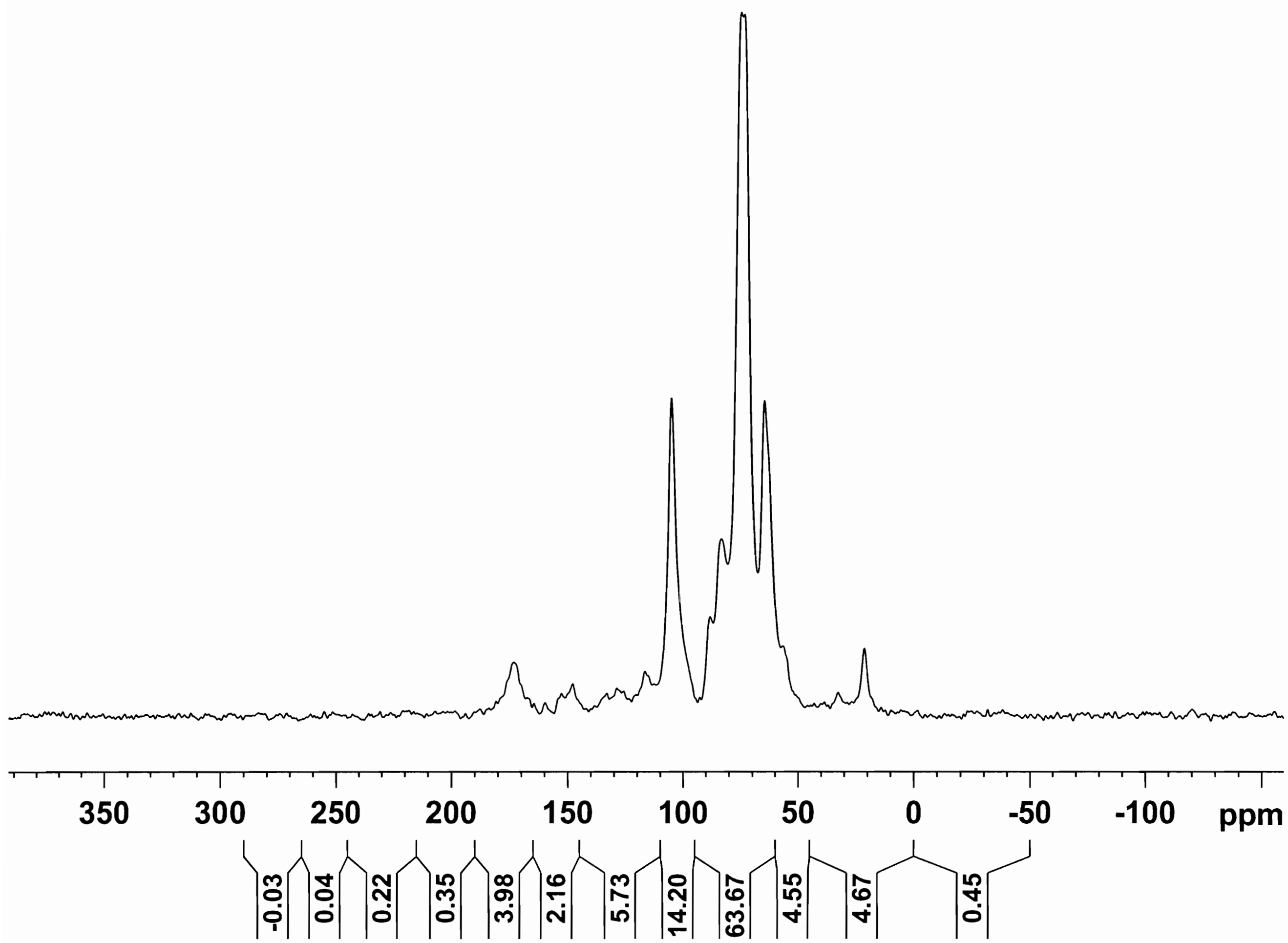
F2 - Acquisition Parameters
Date_ 20091111
Time 22.01
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cp.99.WCH
TD 1024
SOLVENT
NS 2000
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 2048
DW 18.000 usec
DE 17.00 usec
TE 292.5 K
D1 3.00000000 sec
TD0 8

======== CHANNEL f1 ========
NUC1 13C
P15 1000.00 usec
PL1 2.40 dB
SFO1 50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.15 usec
P31 6.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3228472 MHz
WDW EM
SSB 0
LB 40.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 304_7B Rep. Support, Treatment 202 kg N/ha, Replicate 3, No Cover Crop
11/13/2009   78.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC304_7B
EXPNO                      1
PROCNO                     1

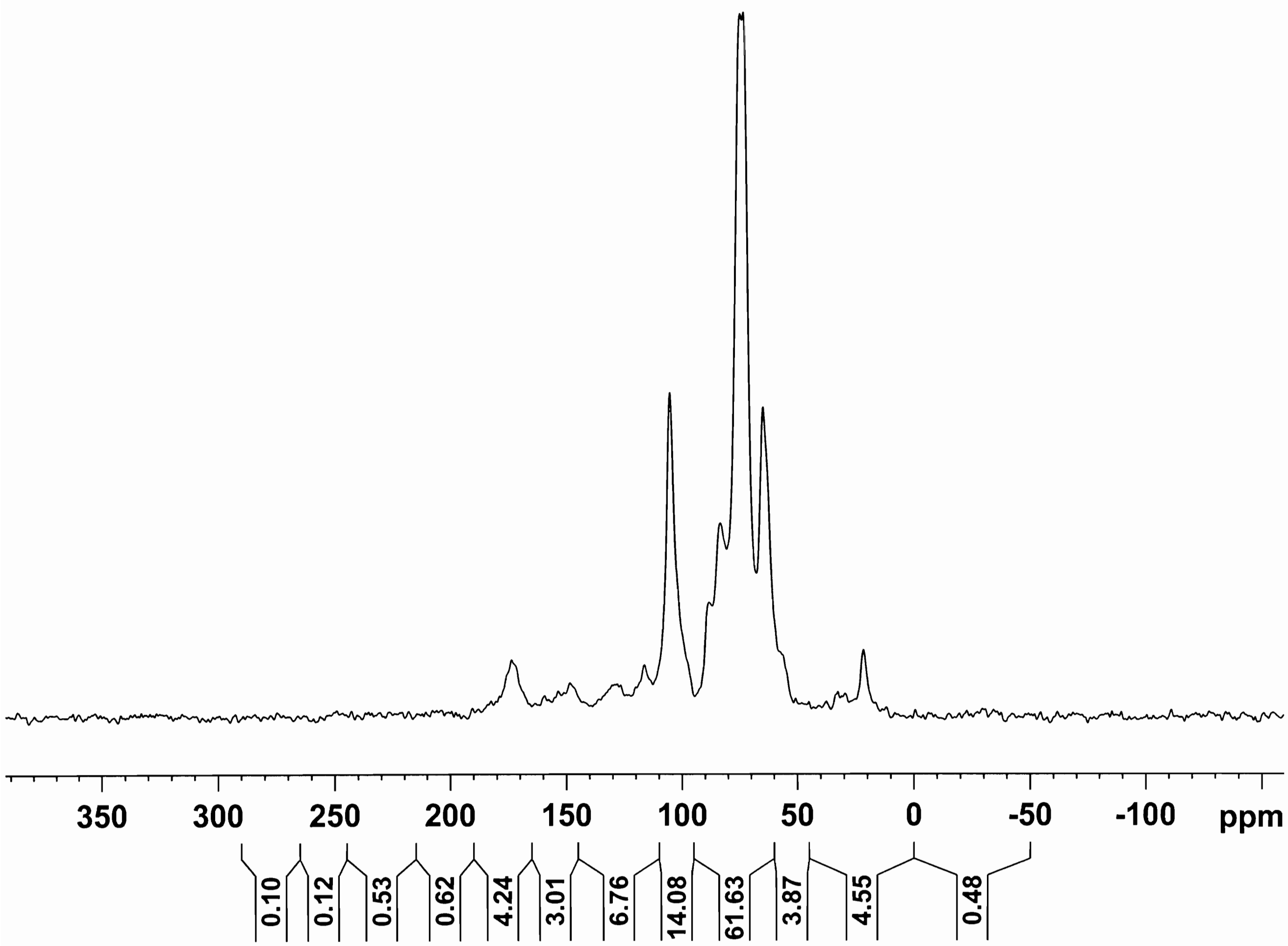
F2 - Acquisition Parameters
Date_             20091113
Time                 11.14
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG         cp.99.WCH
TD                    1024
SOLVENT
NS                    2000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   292.4 K
D1              3.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 406_7B Rep. Support, Treatment 202 kg N/ha, Replicate 4, No Cover Crop
11/12/2009   68.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS. 1 ms contact pulse.




```
Current Data Parameters
NAME     KBSNRate_HSTC406_7B
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_             20091112
Time                  8.55
INSTRUM              spect
PROBHD     4 mm MASxvt BB
PULPROG          cp.99.WCH
TD                    1024
SOLVENT
NS                    2000
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    2048
DW                  18.000 usec
DE                   17.00 usec
TE                   292.3 K
D1              3.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                   13C
P15                1000.00 usec
PL1                   2.40 dB
SFO1            50.3287070 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.15 usec
P31                   6.00 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3228472 MHz
WDW                     EM
SSB                      0
LB                   40.00 Hz
GB                       0
PC                    1.00
```

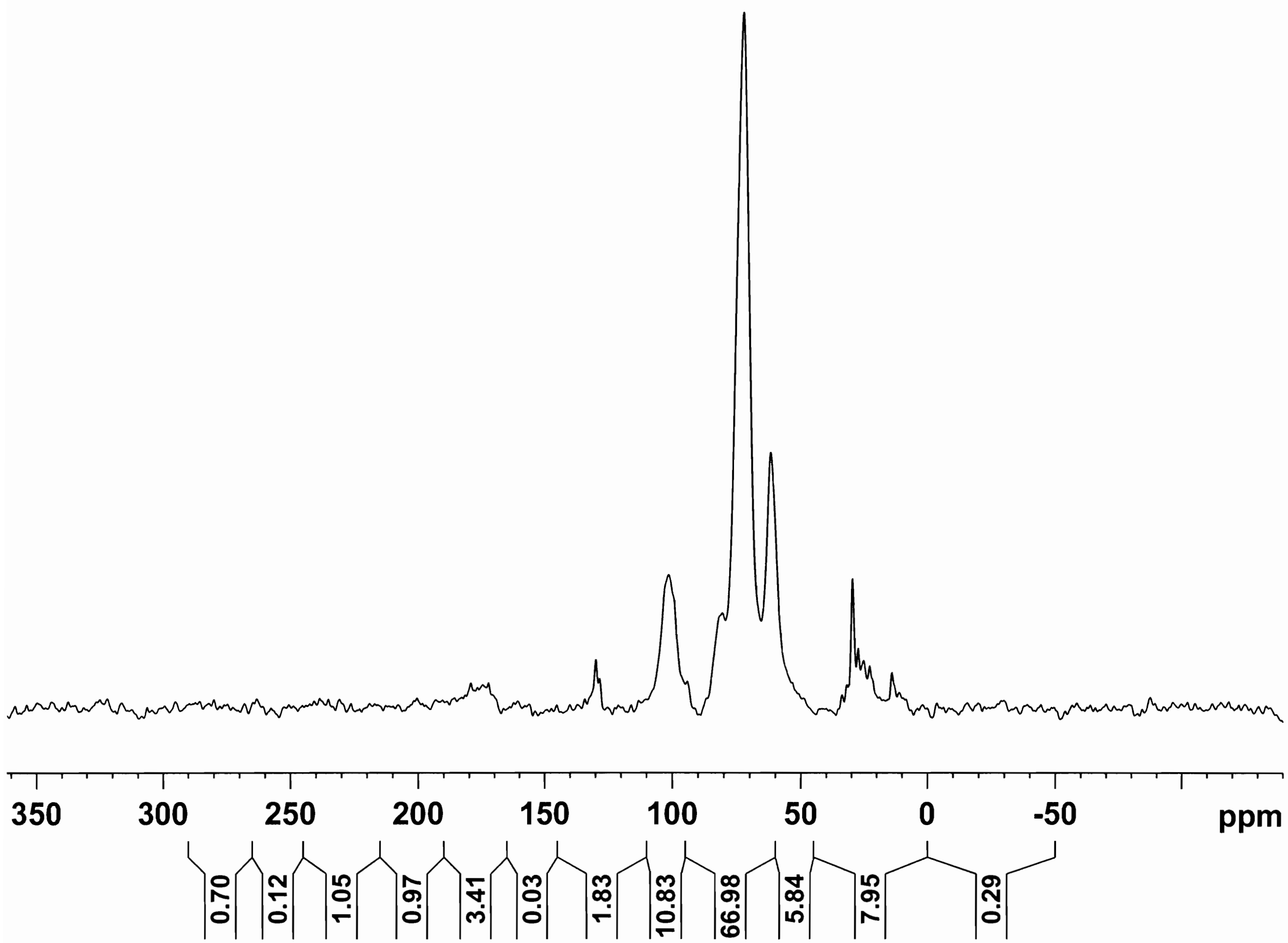
APPENDIX E

^{13}C NMR Direct Polarization Spectra

Solid-state ^{13}C NMR was performed at Rice University using Bruker 200 MHz NMR spectrometer. C-13 NMR direct polarization-magic angle spinning spectra were collected for grain and leaf and stem samples from the N Rate Experiment (Figure E1).

FIGURES Pg #

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Grain, Treatment 0 kg N/ha, Replicate 1, Cover Crop
02/16/2008   109.8 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain101_1A	
EXPNO	3	
PROCNO	3	

F2 - Acquisition Parameters

Date_	20080216	
Time	5.42	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	hpdec	
TD	1024	
SOLVENT		
NS	12288	
DS	2	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	14596.5	
DW	19.800	usec
DE	20.00	usec
TE	698.6	K
D1	3.00000000	sec
TD0	24	

======== CHANNEL f1 ========

NUC1	13C	
P1	0.95	usec
PL1	1.40	dB
SFO1	50.3285161	MHz

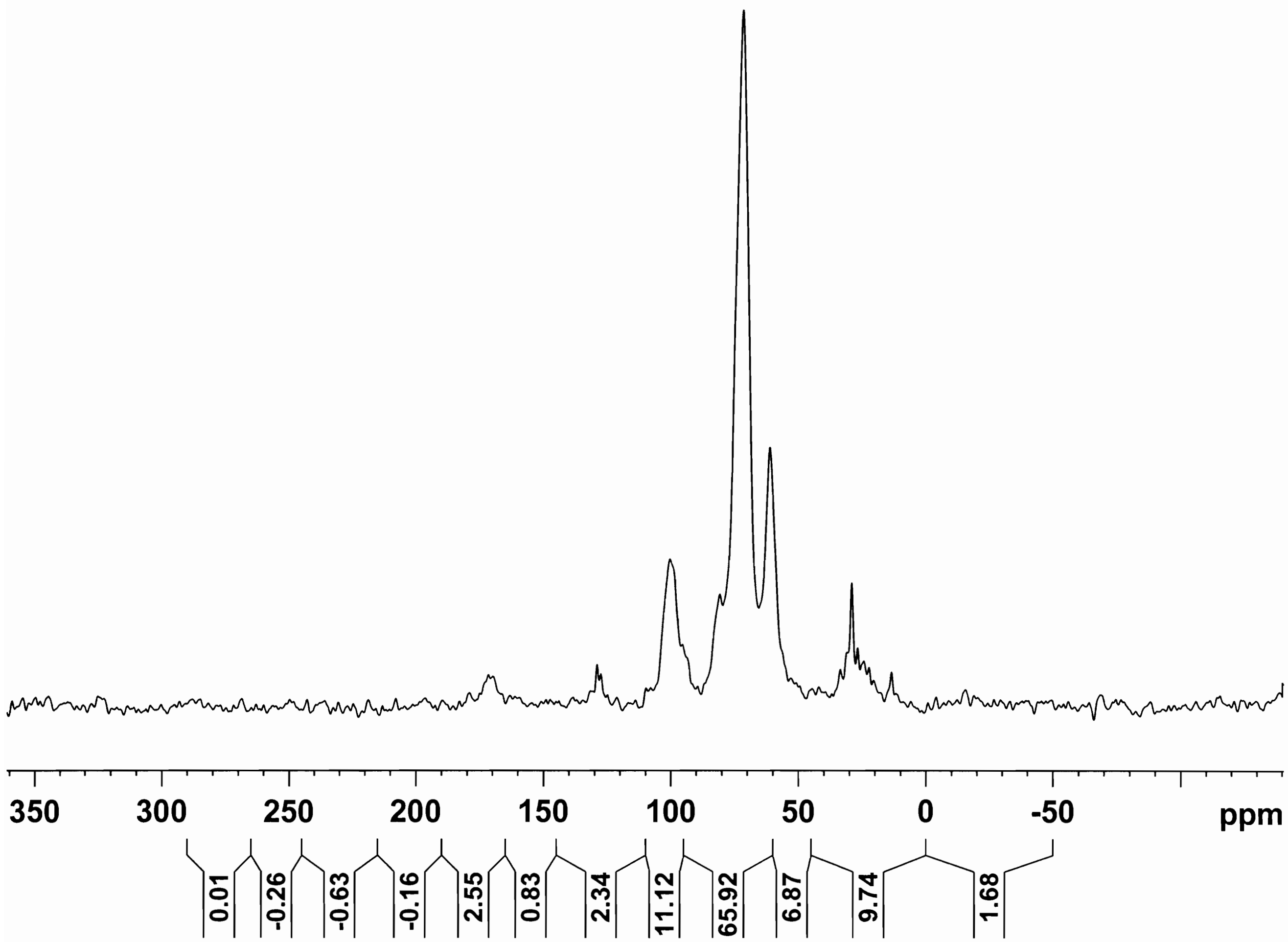
======== CHANNEL f2 ========

NUC2	1H	
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3229361	MHz
WDW	EM	
SSB	0	
LB	50.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Grain, Treatment 34 kg N/ha, Replicate 1, Cover Crop
03/04/2008   103.4 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain107_2A	
EXPNO	3	
PROCNO	2	

F2 - Acquisition Parameters

Date_	20080304	
Time	13.19	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	hpdec	
TD	1024	
SOLVENT		
NS	12288	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	1448.2	
DW	19.800	usec
DE	6.00	usec
TE	698.1	K
D1	3.00000000	sec
TD0	24	

======== CHANNEL f1 ========

NUC1	13C	
P1	0.94	usec
PL1	1.90	dB
SFO1	50.3285161	MHz

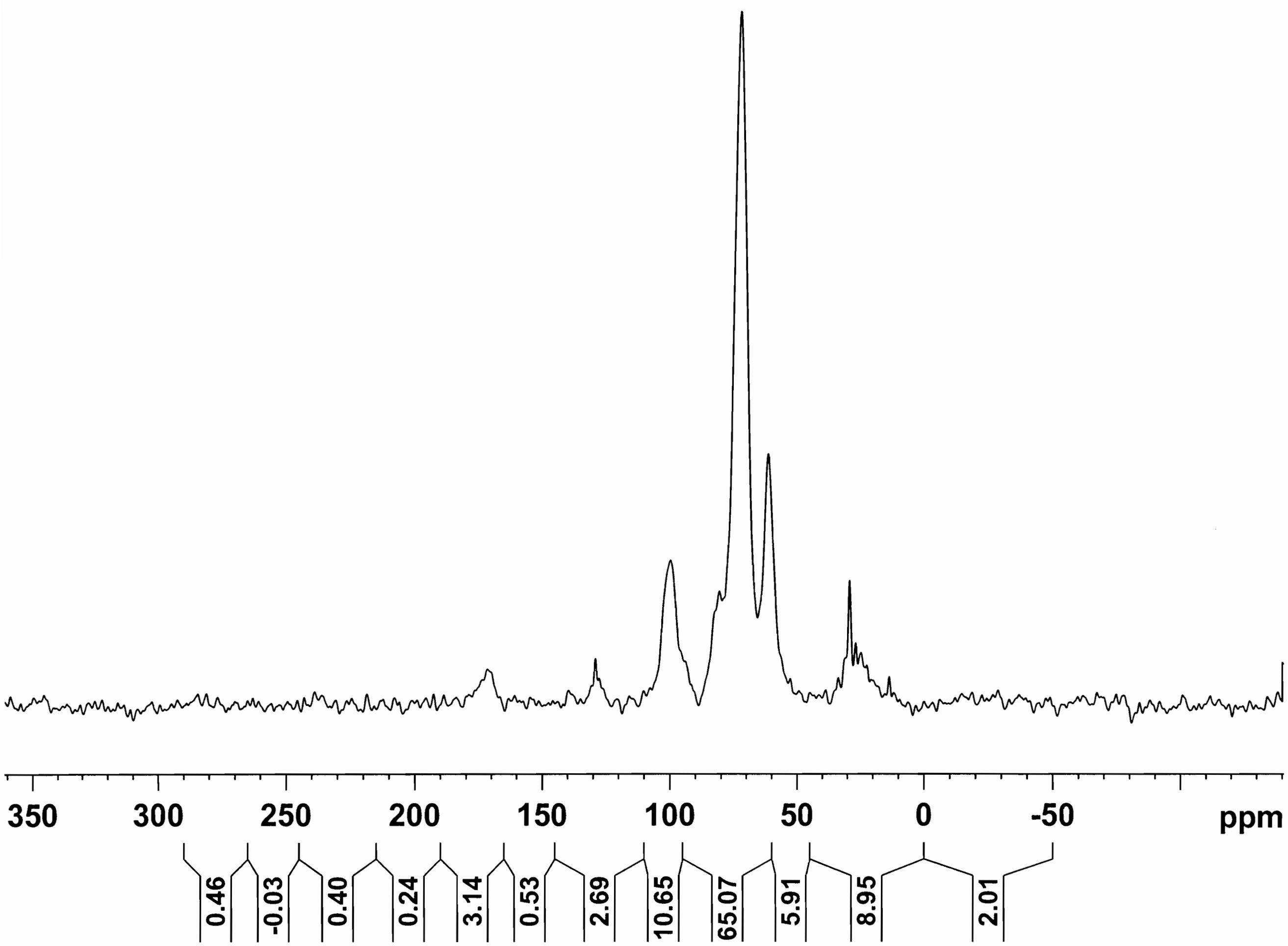
======== CHANNEL f2 ========

NUC2	1H	
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3229682	MHz
WDW	EM	
SSB	0	
LB	50.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Grain, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/05/2008 103.3 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain106_3A
EXPNO	3
PROCNO	2

F2 - Acquisition Parameters

Date_	20080305
Time	4.43
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2580.3
DW	19.800 usec
DE	6.00 usec
TE	697.8 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

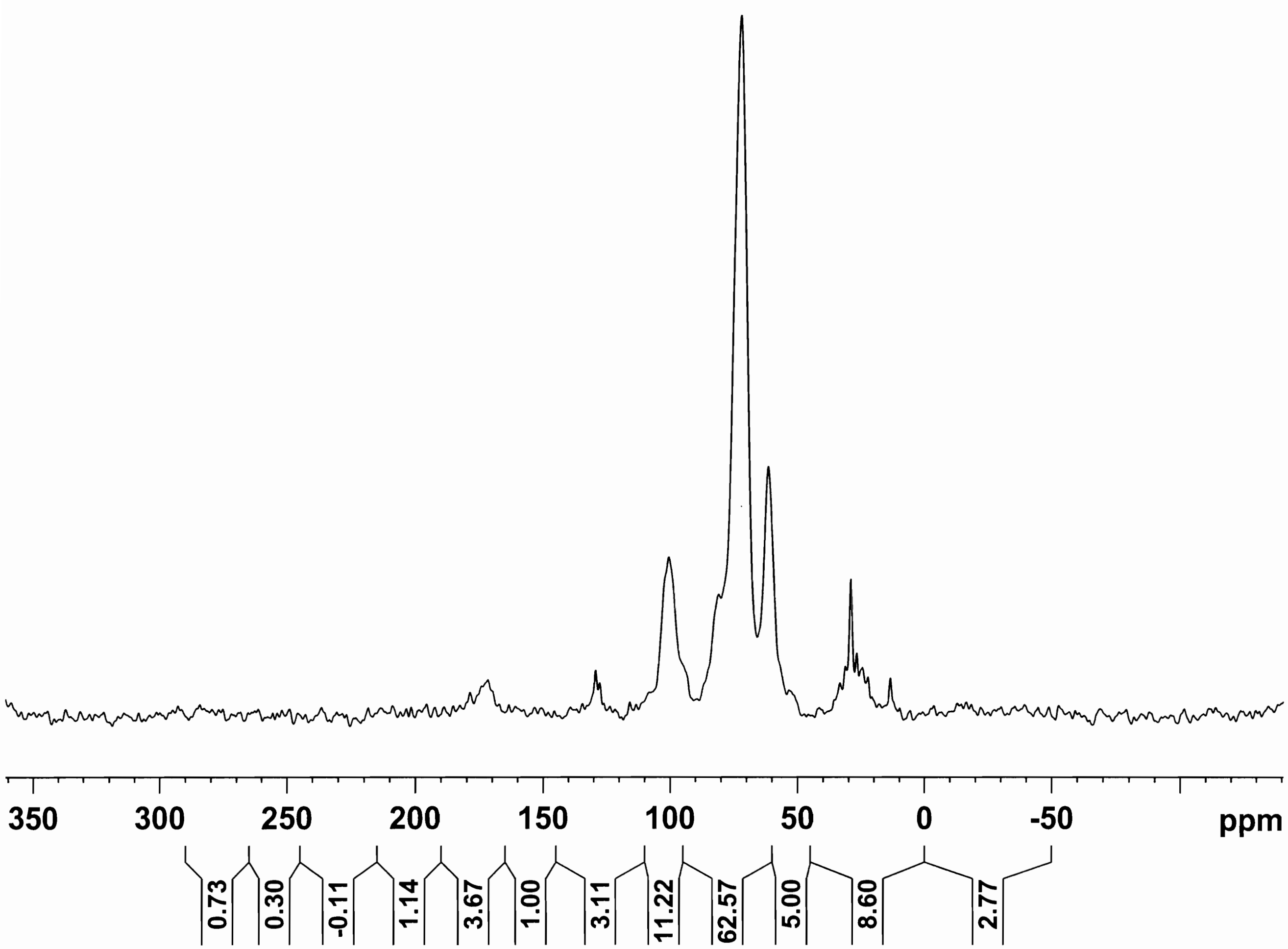
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229682 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Grain, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/05/2008   111.2 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.

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Current Data Parameters
NAME      KBSNRate_Grain102_4A
EXPNO                        3
PROCNO                       2

F2 - Acquisition Parameters
Date_             20080305
Time                 21.29
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG              hpdec
TD                    1024
SOLVENT
NS                   12288
DS                       0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                  2580.3
DW                  19.800 usec
DE                    6.00 usec
TE                   698.0 K
D1              3.00000000 sec
TD0                     24

======== CHANNEL f1 ========
NUC1                   13C
P1                    0.94 usec
PL1                   1.90 dB
SFO1            50.3285161 MHz

======== CHANNEL f2 ========
NUC2                    1H
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229682 MHz
WDW                     EM
SSB                      0
LB                   50.00 Hz
GB                       0
PC                    1.00
```
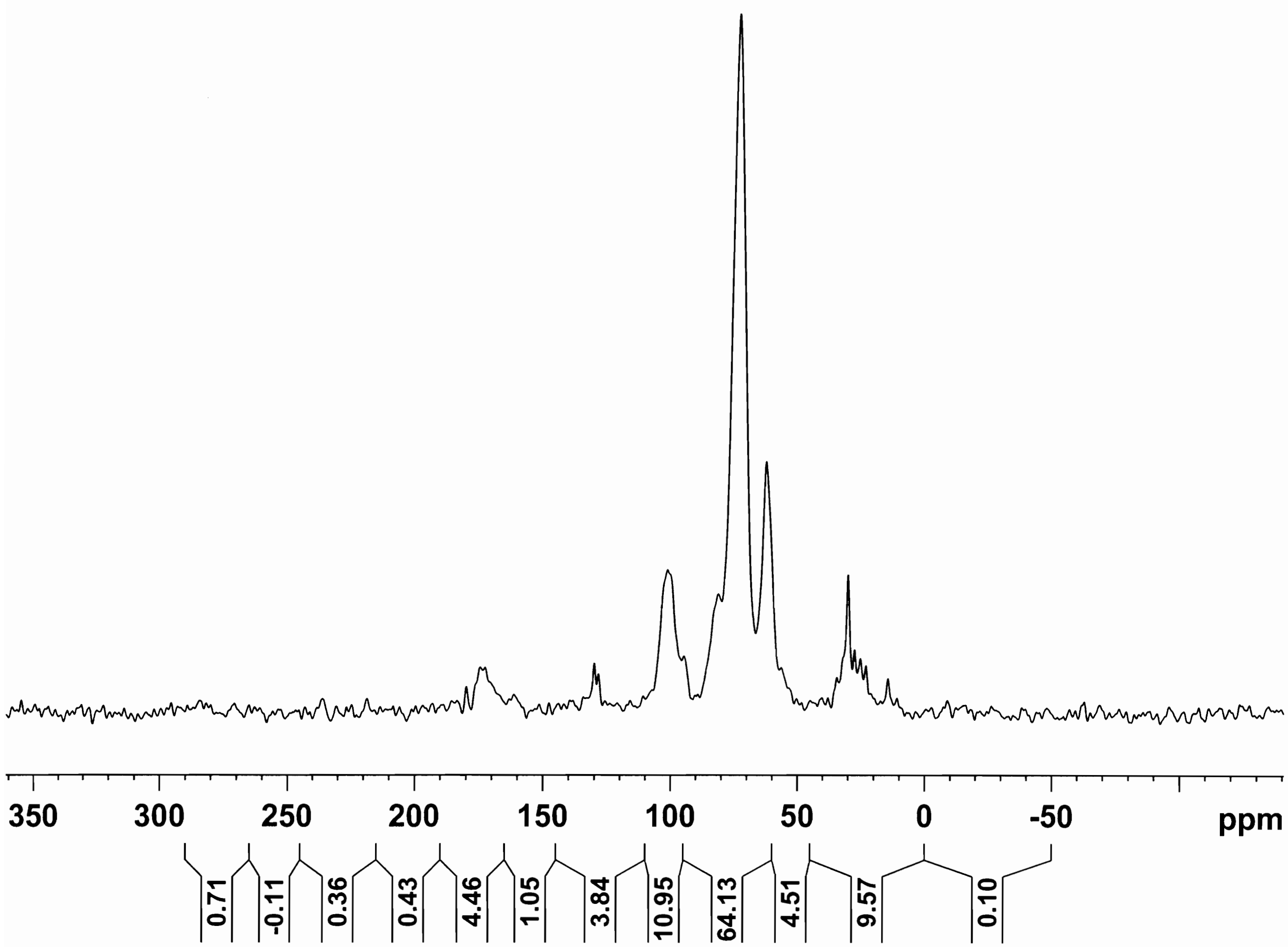

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Grain, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/06/2008 103.9 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_Grain104_5A
EXPNO 3
PROCNO 2

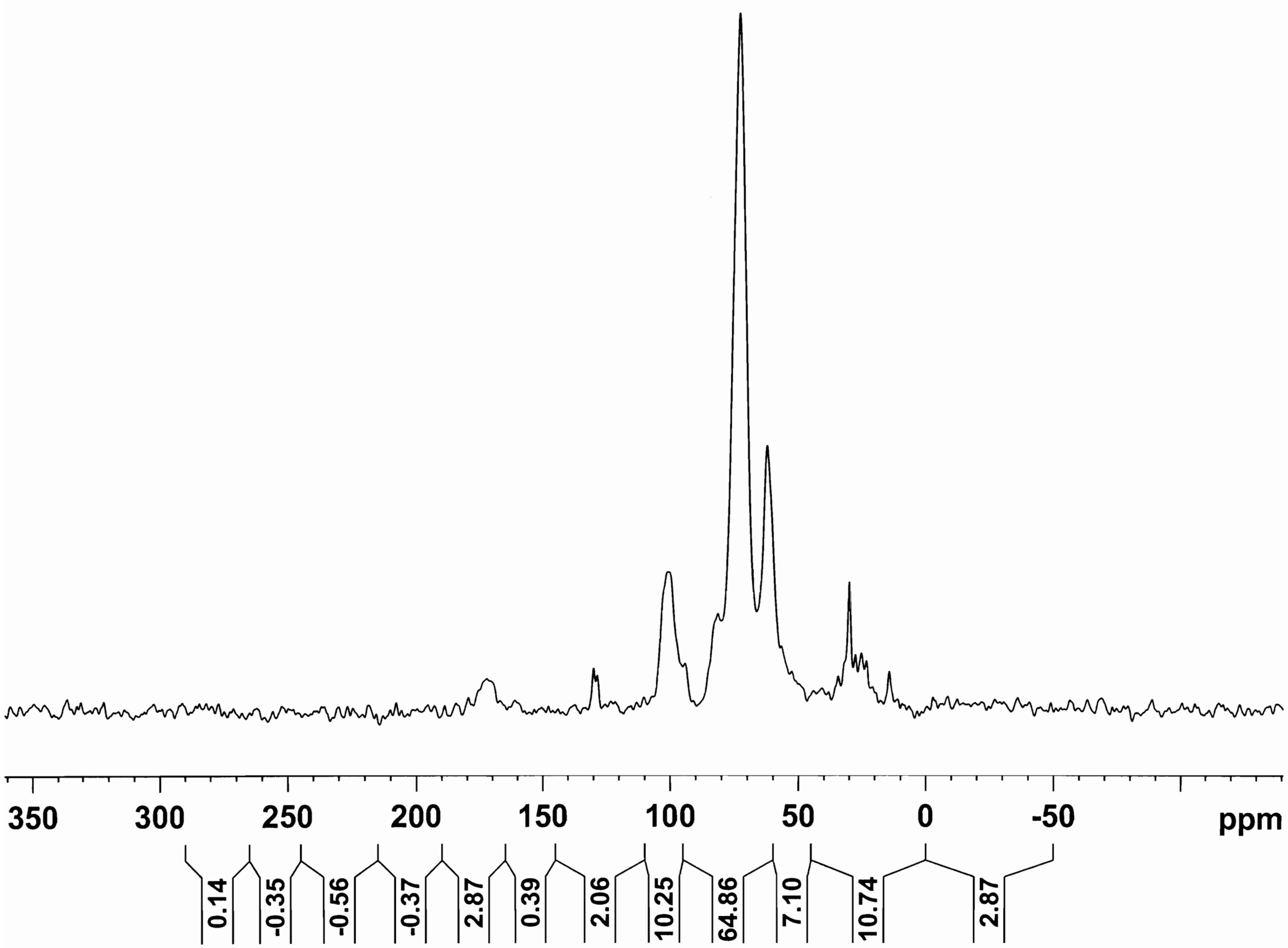
F2 - Acquisition Parameters
Date_ 20080306
Time 15.54
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 695.0 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Grain, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/07/2008 102.7 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain103_6A
EXPNO	3
PROCNO	2

F2 - Acquisition Parameters

Date_	20080307
Time	7.10
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2580.3
DW	19.800 usec
DE	6.00 usec
TE	694.1 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

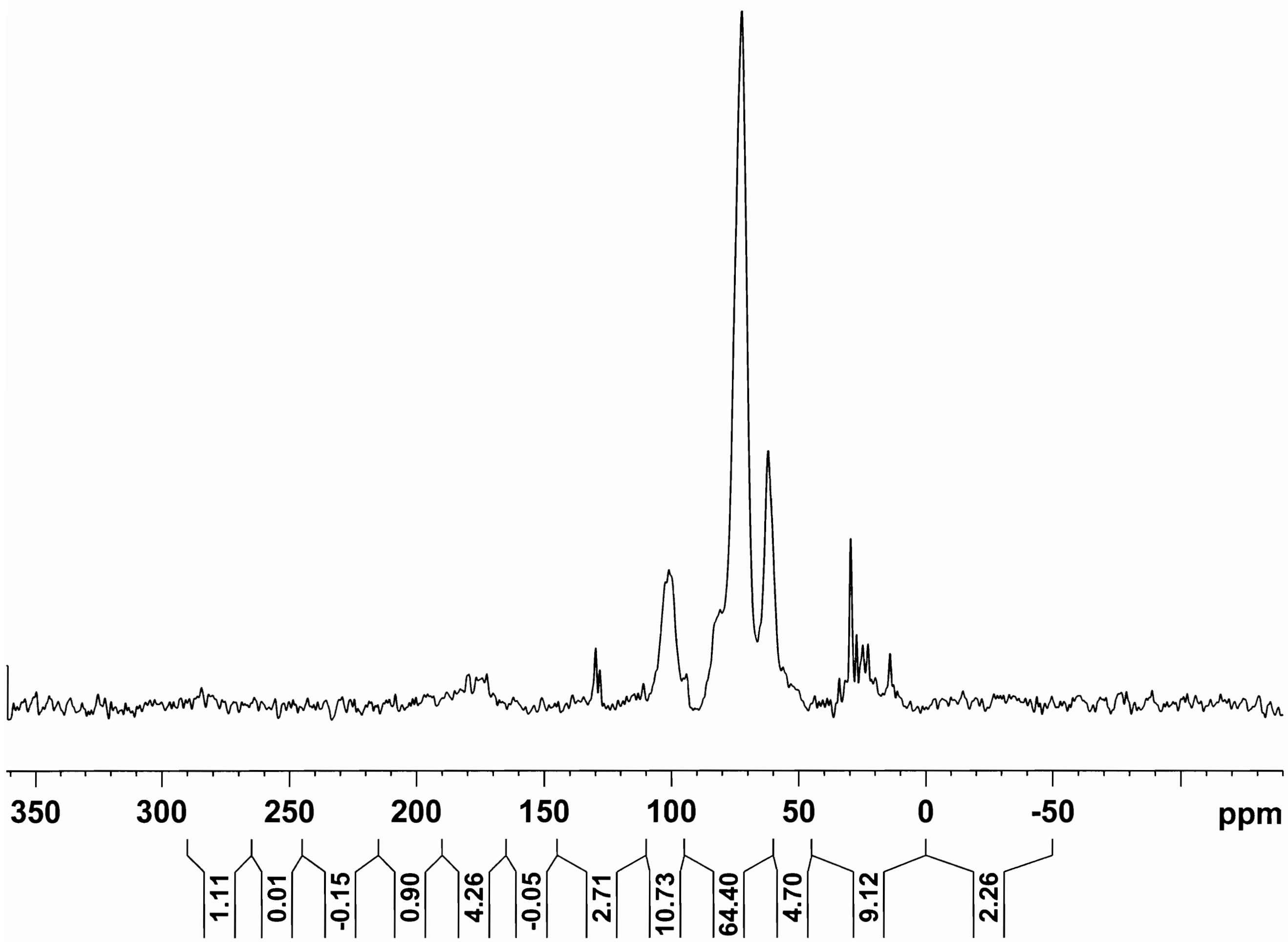
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

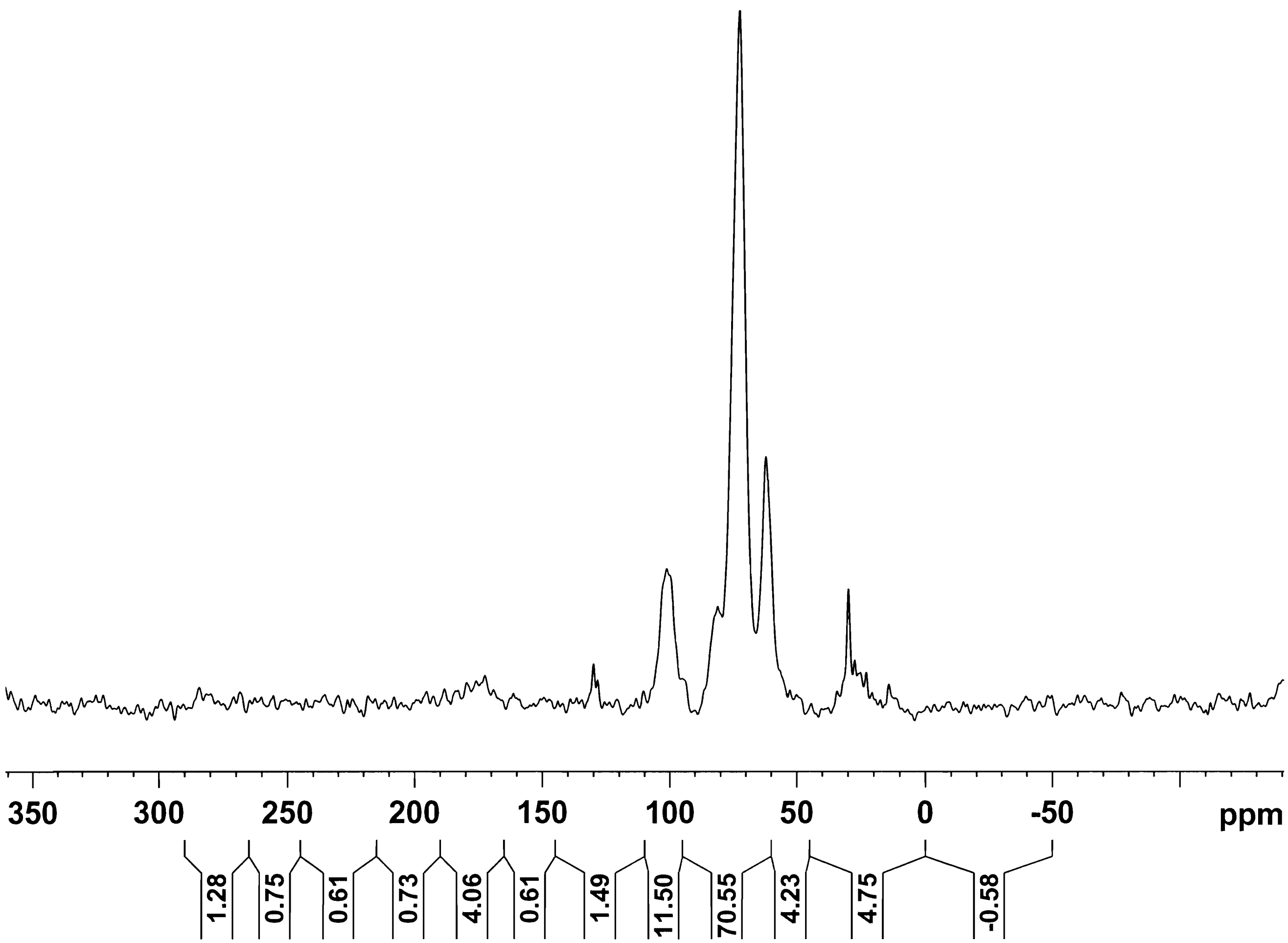
SI	16384
SF	50.3229682 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Grain, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/14/2008   101.4 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.




```
Current Data Parameters
NAME     KBSNRate_Grain105_7A
EXPNO                   2
PROCNO                  2

F2 - Acquisition Parameters
Date_            20080214
Time                20.54
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG             hpdec
TD                   1024
SOLVENT
NS                  12288
DS                      2
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                14596.5
DW                 19.800 usec
DE                  20.00 usec
TE                  696.1 K
D1             3.00000000 sec
TD0                    24

======== CHANNEL f1 ========
NUC1                  13C
P1                   0.95 usec
PL1                  1.40 dB
SFO1           50.3285161 MHz

======== CHANNEL f2 ========
NUC2                   1H
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229361 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Grain, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/13/2008   103.9 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_Grain101_1B
EXPNO 3
PROCNO 2

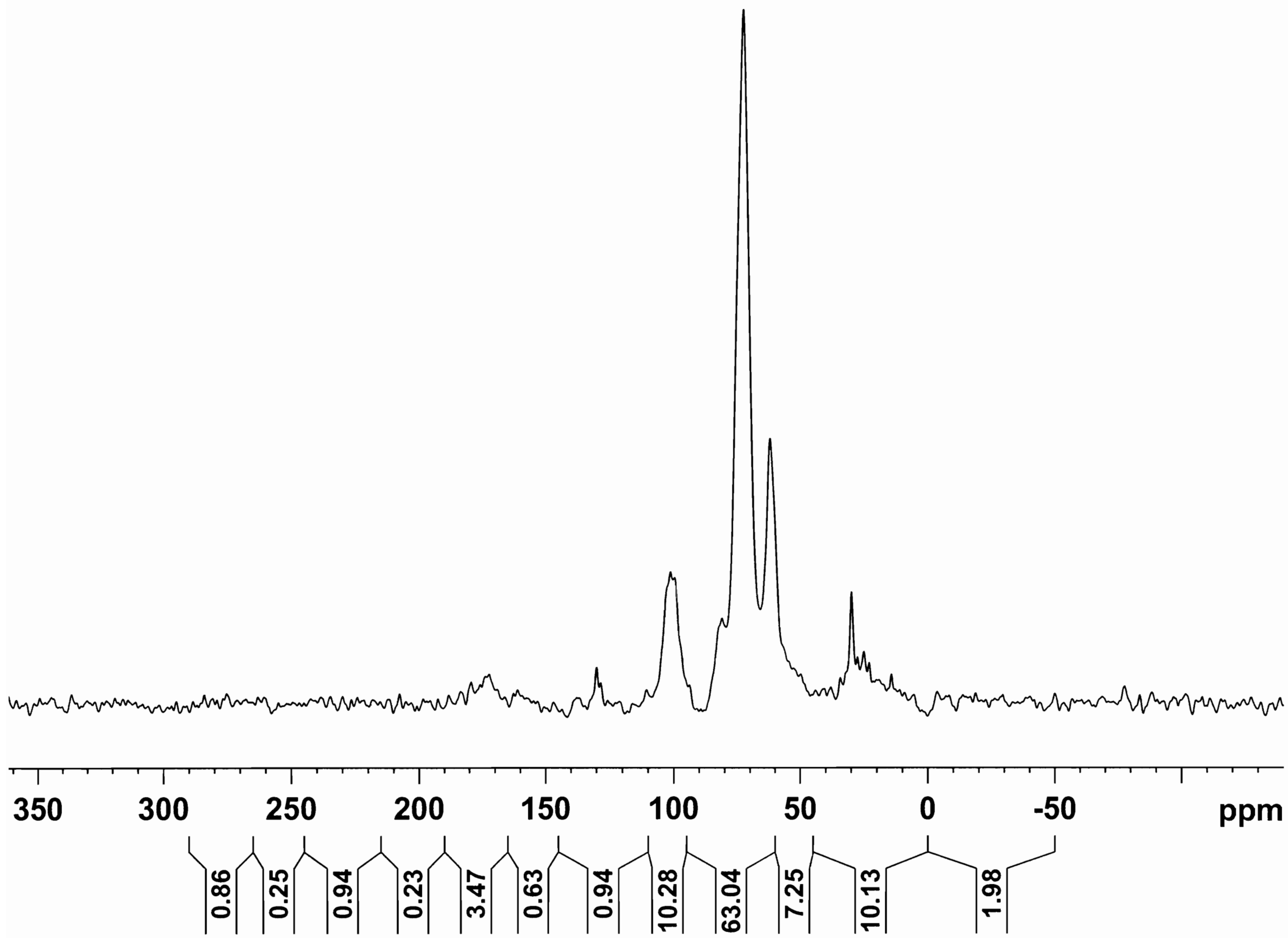
F2 - Acquisition Parameters
Date_ 20080313
Time 21.54
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 698.0 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

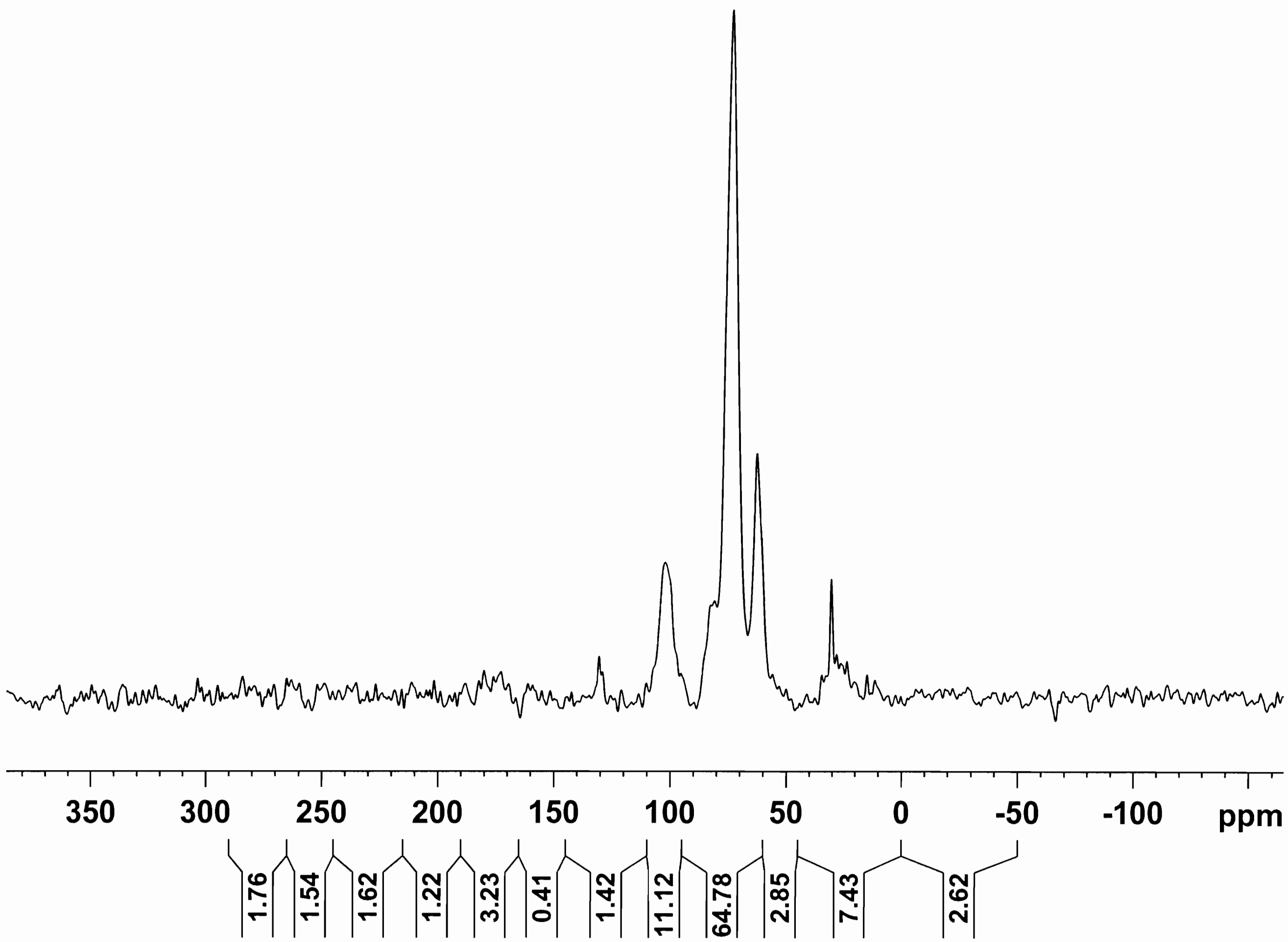
F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Grain, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
06/29/2008   102.1 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.




```
Current Data Parameters
NAME      KBSNRate_Grain107_2B
EXPNO                        3
PROCNO                       2

F2 - Acquisition Parameters
Date_             20080629
Time                 13.12
INSTRUM              spect
PROBHD    4 mm MASxvt BB
PULPROG              hpdec
TD                    1024
SOLVENT
NS                   12288
DS                       2
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                    4096
DW                  19.800 usec
DE                    6.00 usec
TE                   697.0 K
D1              3.00000000 sec
TD0                     24

======== CHANNEL f1 ========
NUC1                   13C
P1                    0.94 usec
PL1                   1.90 dB
SFO1            50.3285161 MHz

======== CHANNEL f2 ========
NUC2                    1H
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229324 MHz
WDW                     EM
SSB                      0
LB                   50.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Grain, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/16/2008   100.5 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain106_3B
EXPNO	3
PROCNO	3

F2 - Acquisition Parameters

Date_	20080616
Time	22.45
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	2
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	4096
DW	18.000 usec
DE	6.00 usec
TE	697.6 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

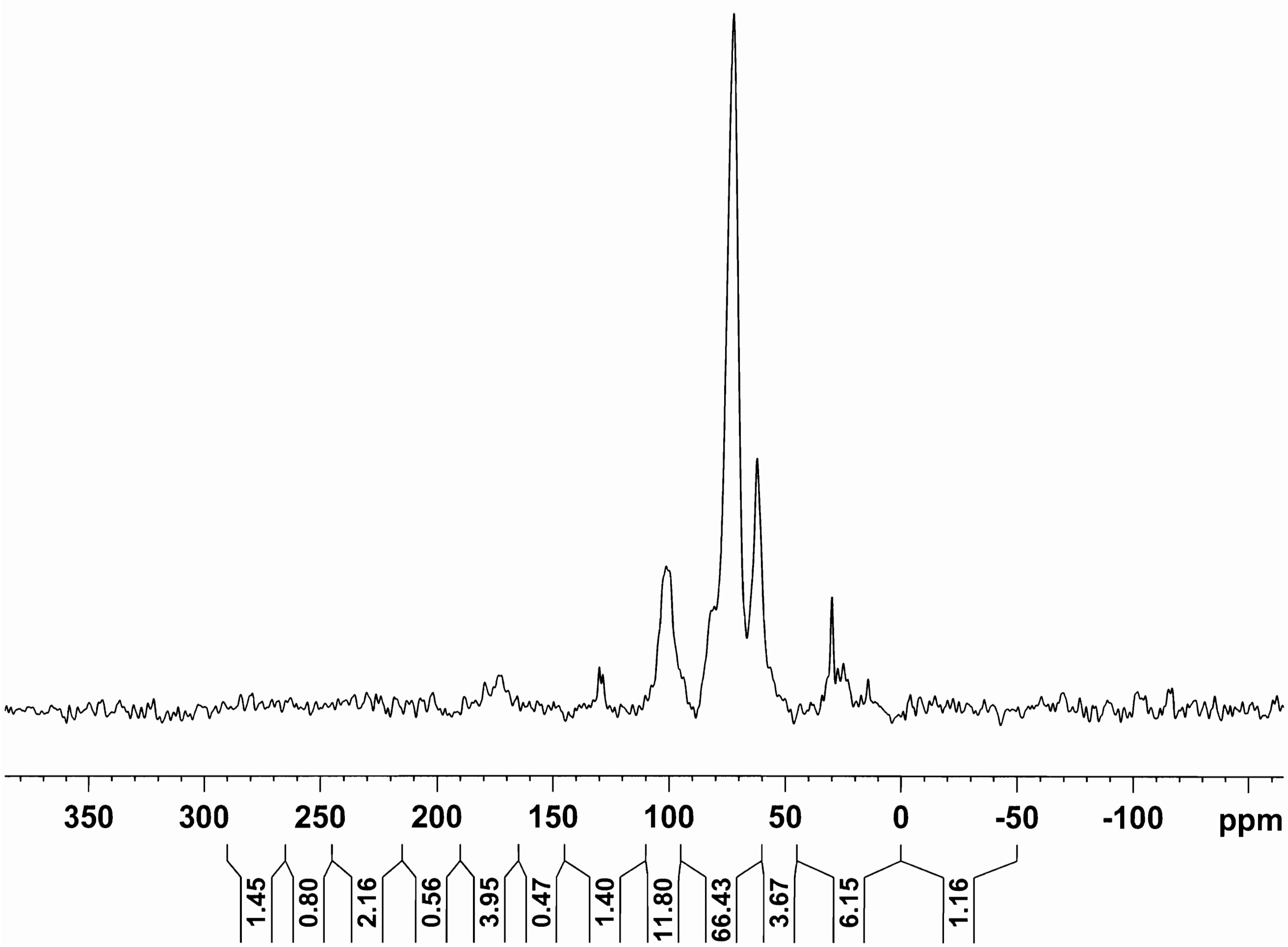
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229323 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Grain, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/14/2008   105.1 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME   KBSNRate_Grain102_4B
EXPNO   3
PROCNO   3

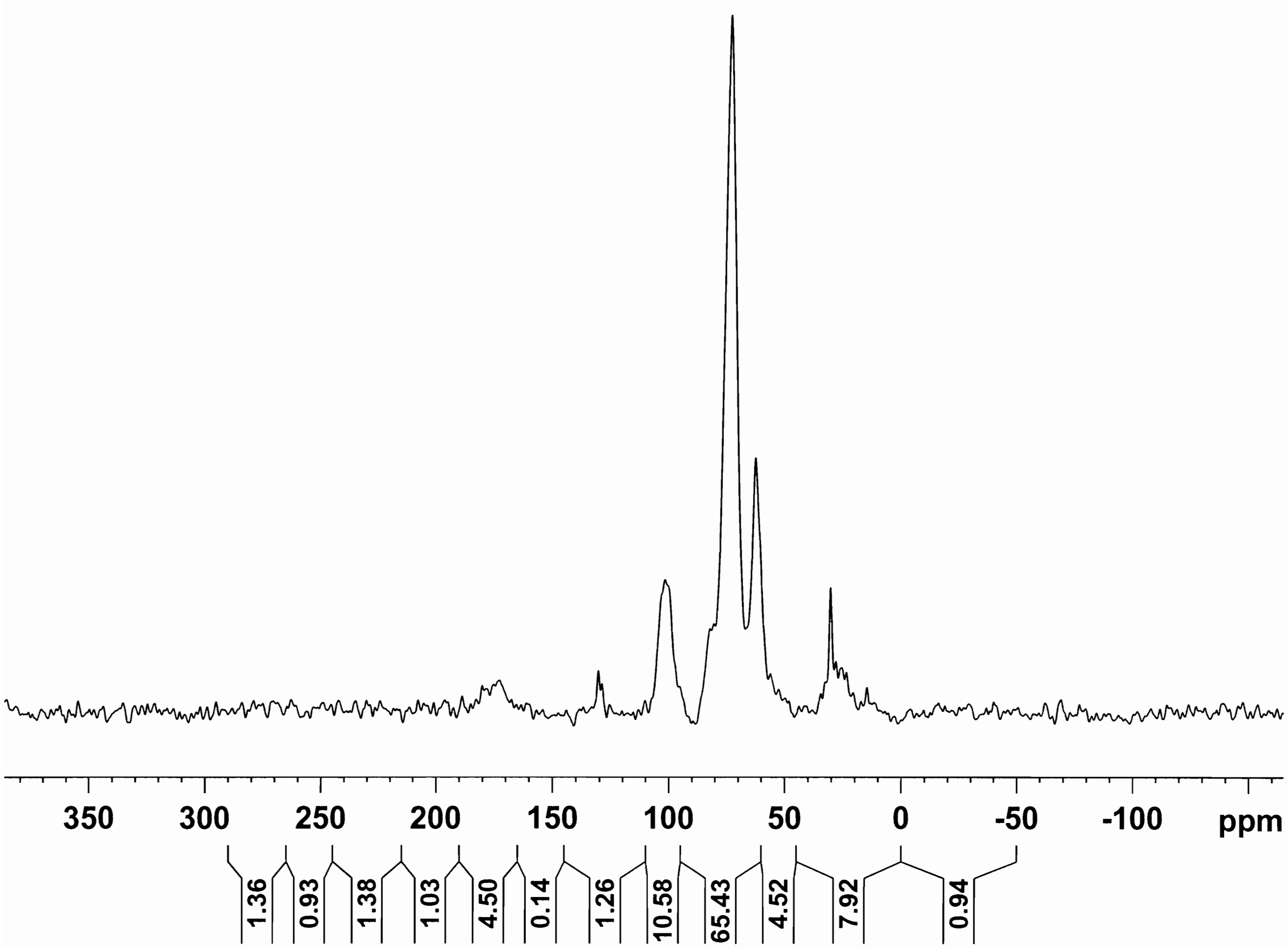
F2 - Acquisition Parameters
Date_   20080614
Time   14.49
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   hpdec
TD   1024
SOLVENT
NS   12288
DS   2
SWH   27777.777 Hz
FIDRES   27.126736 Hz
AQ   0.0185000 sec
RG   2580.3
DW   18.000 usec
DE   6.00 usec
TE   697.6 K
D1   3.00000000 sec
TD0   24

======== CHANNEL f1 ========
NUC1   13C
P1   0.94 usec
PL1   1.90 dB
SFO1   50.3285161 MHz

======== CHANNEL f2 ========
NUC2   1H
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229323 MHz
WDW   EM
SSB   0
LB   50.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Grain, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/12/2008   100.6 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain104_5B
EXPNO	3
PROCNO	3

F2 - Acquisition Parameters

Date_	20080612
Time	20.09
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	2
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	2580.3
DW	18.000 usec
DE	6.00 usec
TE	698.3 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

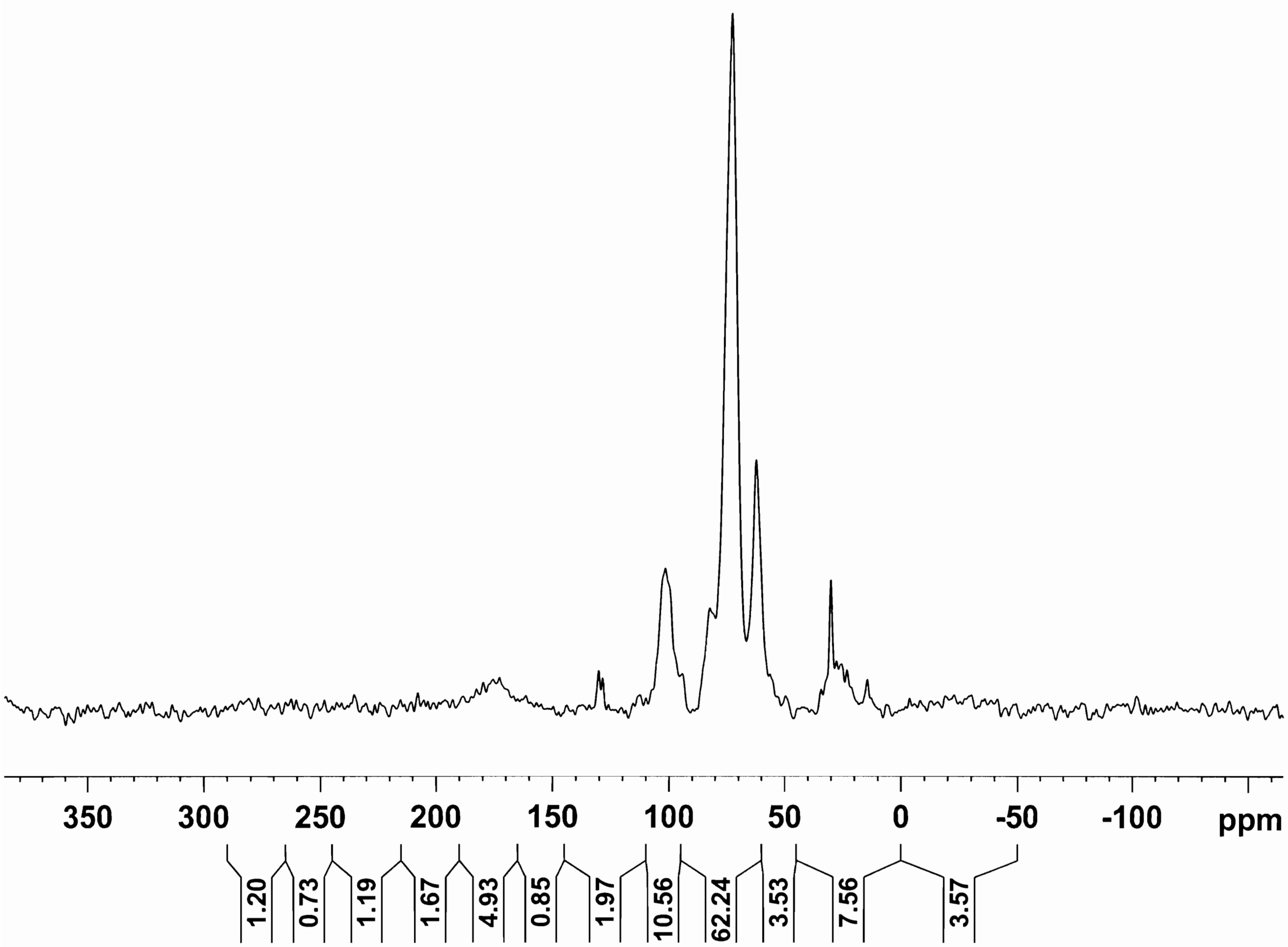
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229323 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Grain, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/11/2008 102.1 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain103_6B
EXPNO	3
PROCNO	3

F2 - Acquisition Parameters

Date_	20080611
Time	23.27
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	2
SWH	27777.777 Hz
FIDRES	27.126736 Hz
AQ	0.0185000 sec
RG	1024
DW	18.000 usec
DE	6.00 usec
TE	698.2 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

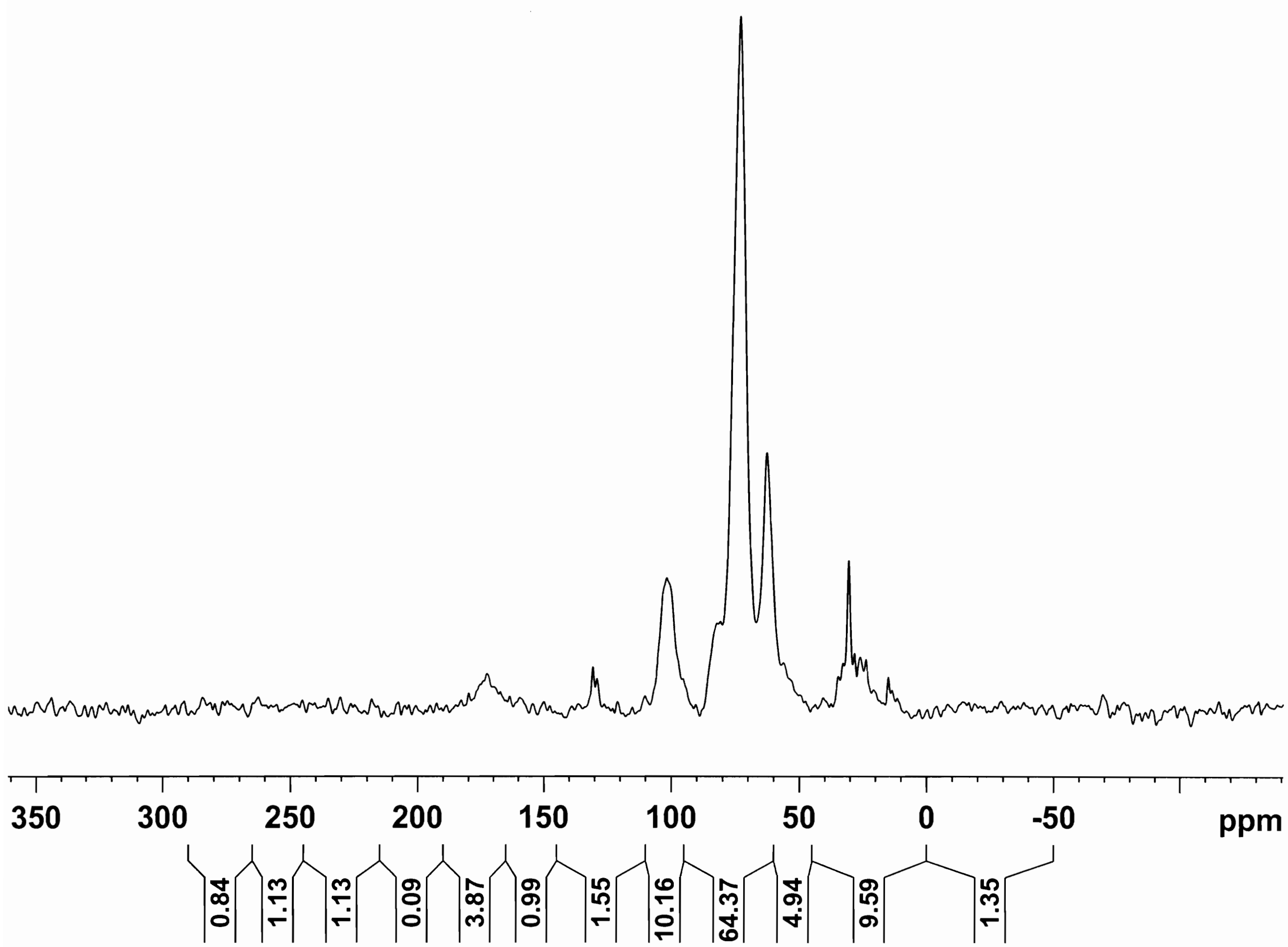
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229323 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Grain, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/14/2008   103.0 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_Grain105_7B	
EXPNO	3	
PROCNO	2	

F2 - Acquisition Parameters

Date_	20080314	
Time	14.38	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	hpdec	
TD	1024	
SOLVENT		
NS	12288	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	2580.3	
DW	19.800	usec
DE	6.00	usec
TE	694.5	K
D1	3.00000000	sec
TD0	24	

======== CHANNEL f1 ========

NUC1	13C	
P1	0.94	usec
PL1	1.90	dB
SFO1	50.3285161	MHz

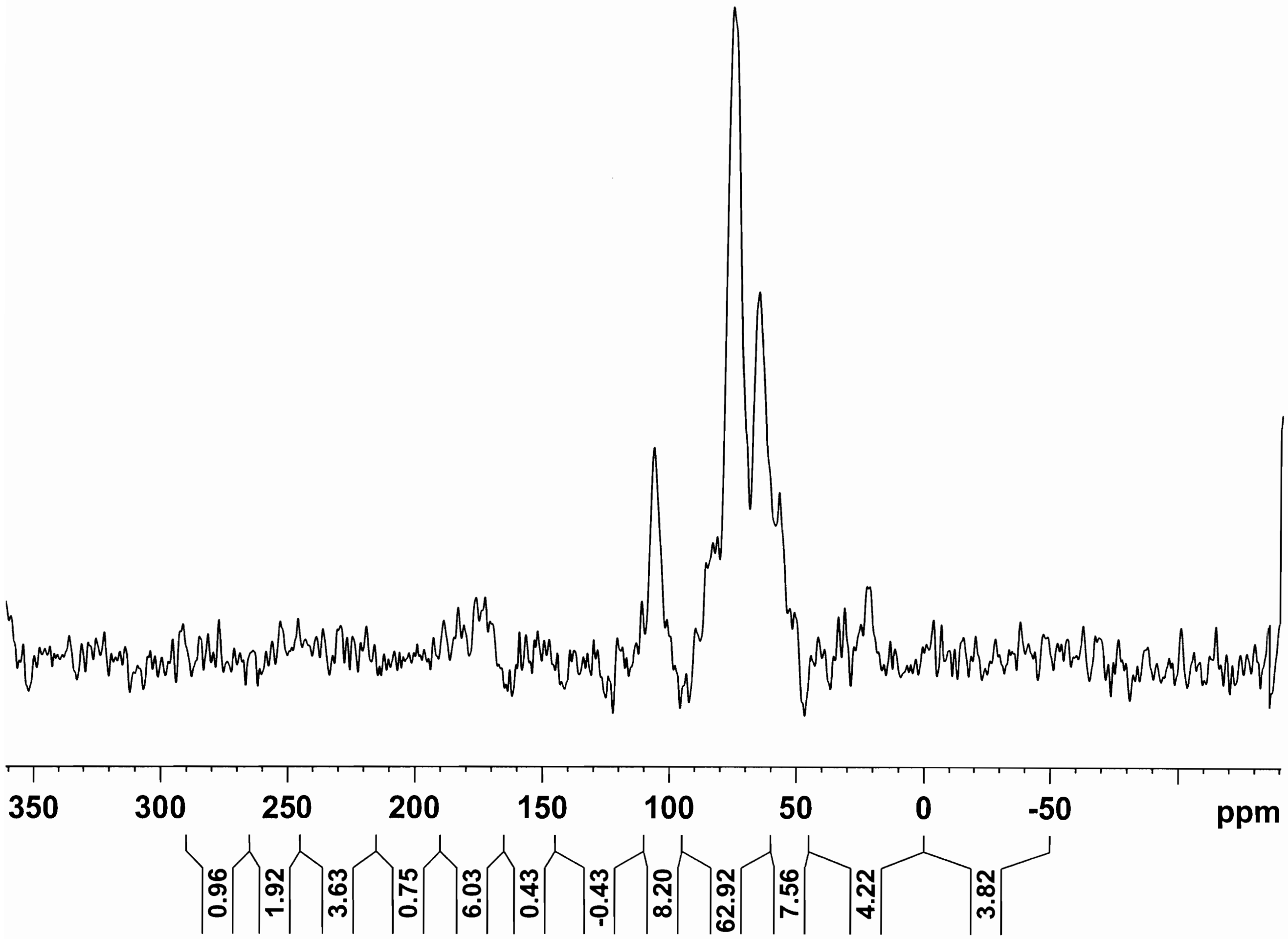
======== CHANNEL f2 ========

NUC2	1H	
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz

F2 - Processing parameters

SI	16384	
SF	50.3229682	MHz
WDW	EM	
SSB	0	
LB	50.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, Cover Crop
03/10/2008   52.8 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_LS101_1A
EXPNO 3
PROCNO 2

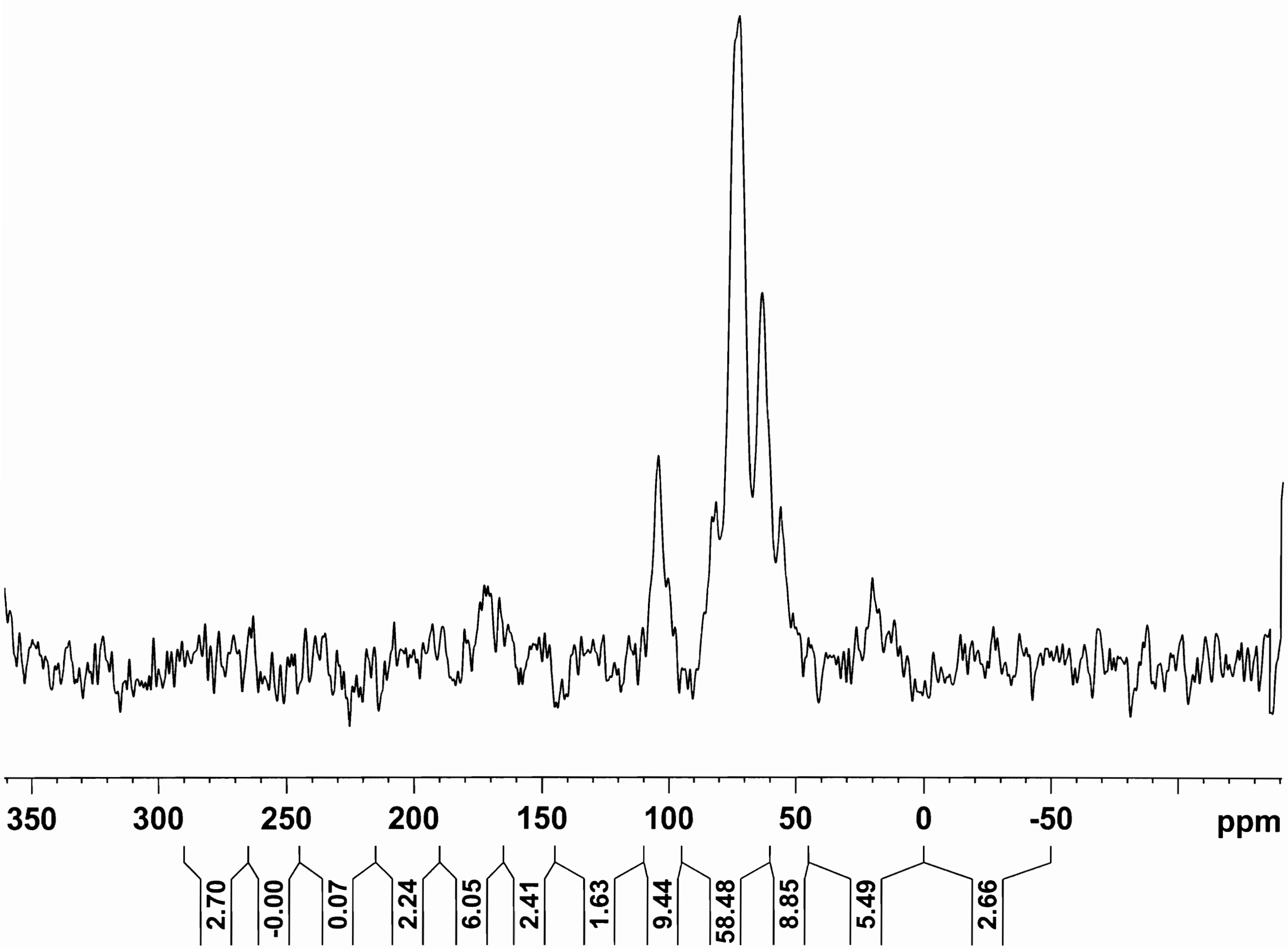
F2 - Acquisition Parameters
Date_ 20080310
Time 20.48
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 694.5 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

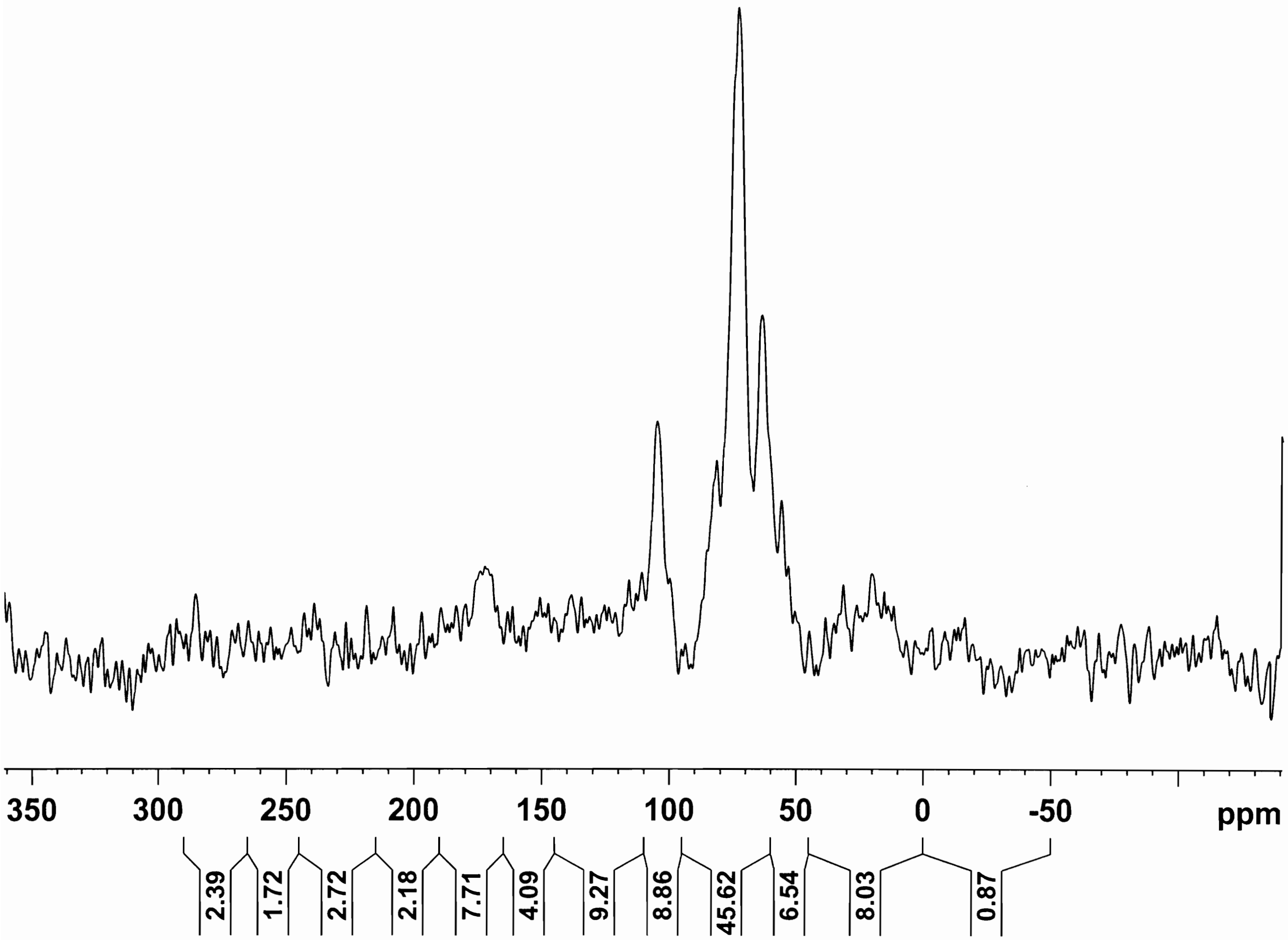
F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, Cover Crop
03/11/2008   53.0 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters		
NAME	KBSNRate_LS107_2A	
EXPNO	3	
PROCNO	2	
F2 - Acquisition Parameters		
Date_	20080311	
Time	19.20	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	hpdec	
TD	1024	
SOLVENT		
NS	12288	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	2580.3	
DW	19.800	usec
DE	6.00	usec
TE	697.2	K
D1	3.00000000	sec
TD0	24	
======== CHANNEL f1 ========		
NUC1	13C	
P1	0.94	usec
PL1	1.90	dB
SFO1	50.3285161	MHz
======== CHANNEL f2 ========		
NUC2	1H	
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz
F2 - Processing parameters		
SI	16384	
SF	50.3229682	MHz
WDW	EM	
SSB	0	
LB	50.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/07/2008 50.3 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_LS106_3A
EXPNO 3
PROCNO 3

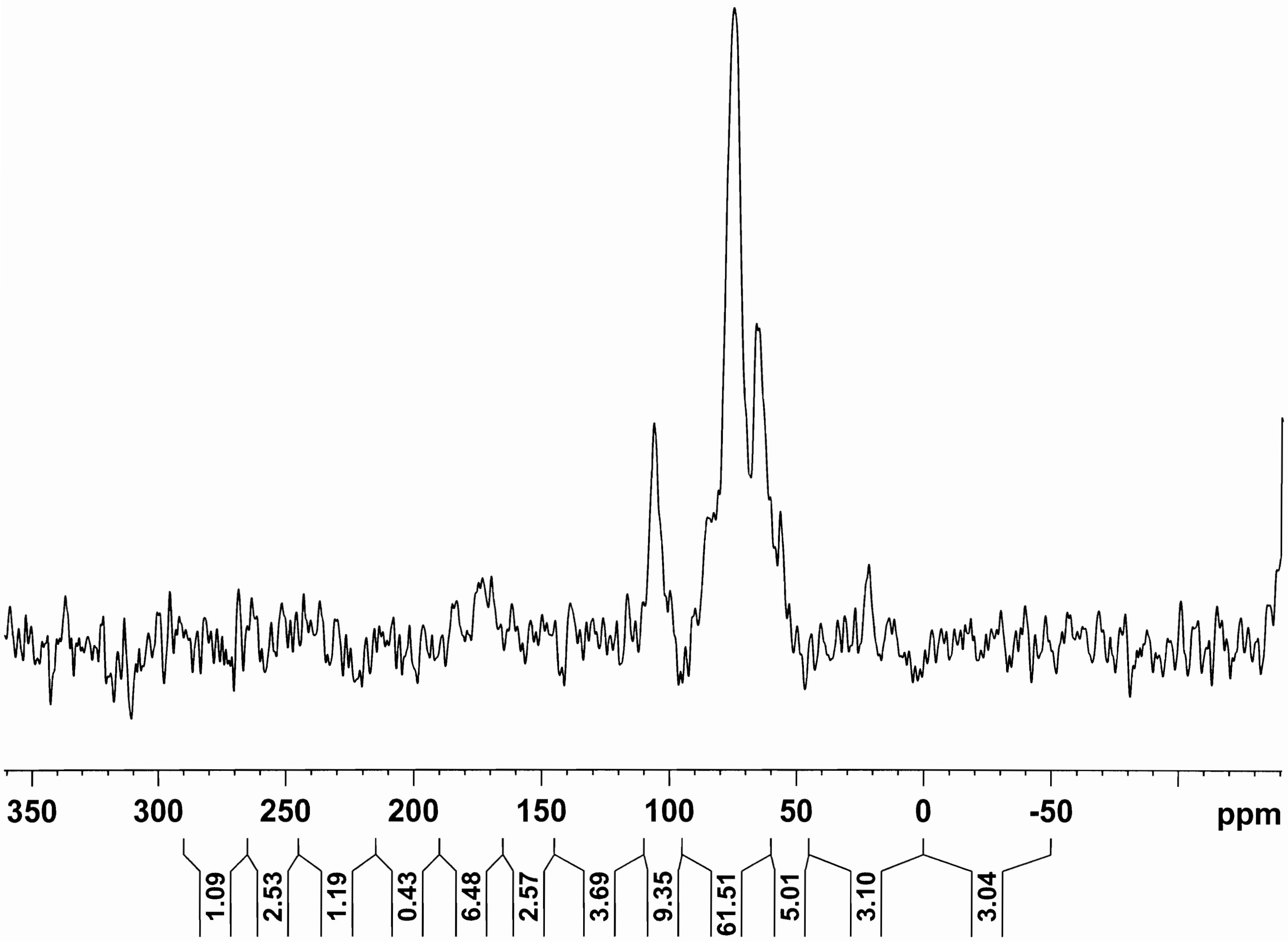
F2 - Acquisition Parameters
Date_ 20080307
Time 22.40
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 694.1 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/08/2008   51.2 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_LS102_4A
EXPNO 3
PROCNO 2

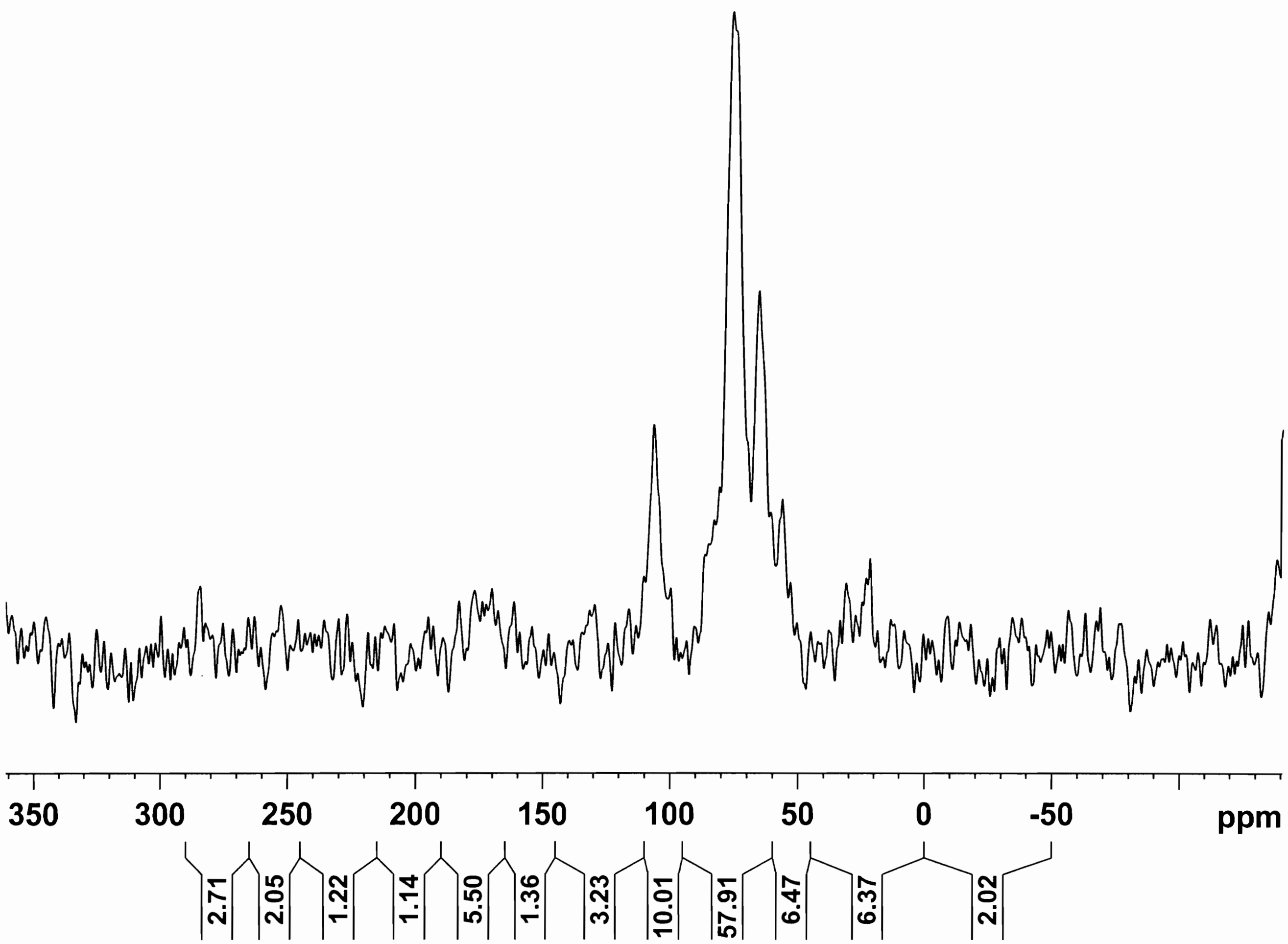
F2 - Acquisition Parameters
Date_ 20080308
Time 14.07
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 694.2 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

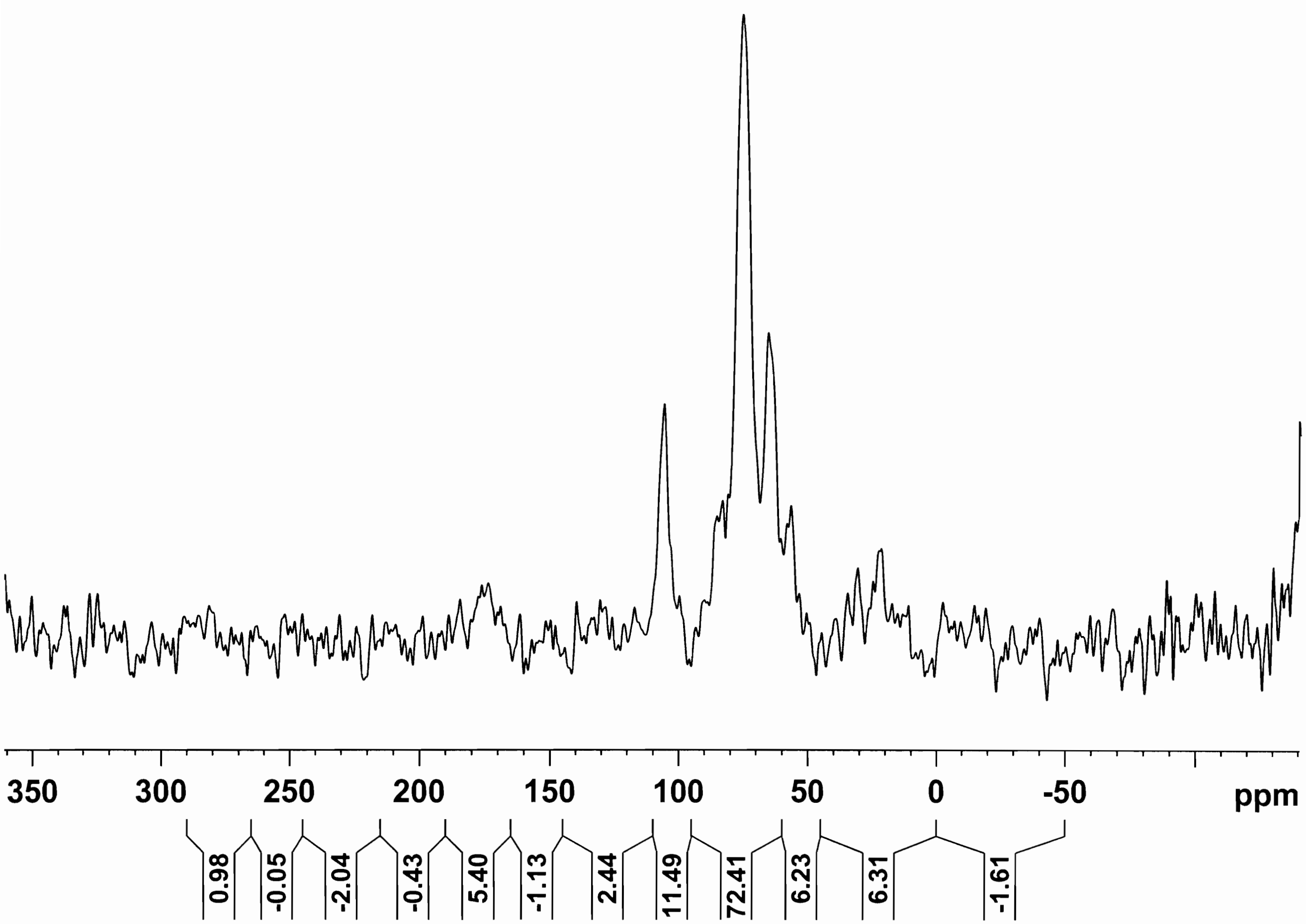
F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/09/2008   49.2 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.




```
Current Data Parameters
NAME      KBSNRate_LS104_5A
EXPNO                     3
PROCNO                    2

F2 - Acquisition Parameters
Date_              20080309
Time                   6.26
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG               hpdec
TD                     1024
SOLVENT
NS                    12288
DS                        0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                   2580.3
DW                   19.800 usec
DE                     6.00 usec
TE                    694.4 K
D1               3.00000000 sec
TD0                      24

======== CHANNEL f1 ========
NUC1                    13C
P1                     0.94 usec
PL1                    1.90 dB
SFO1            50.3285161 MHz

======== CHANNEL f2 ========
NUC2                     1H
PL2                    6.00 dB
PL12                   3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229682 MHz
WDW                      EM
SSB                       0
LB                    50.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/09/2008   48.2 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_LS103_6A
EXPNO 3
PROCNO 2

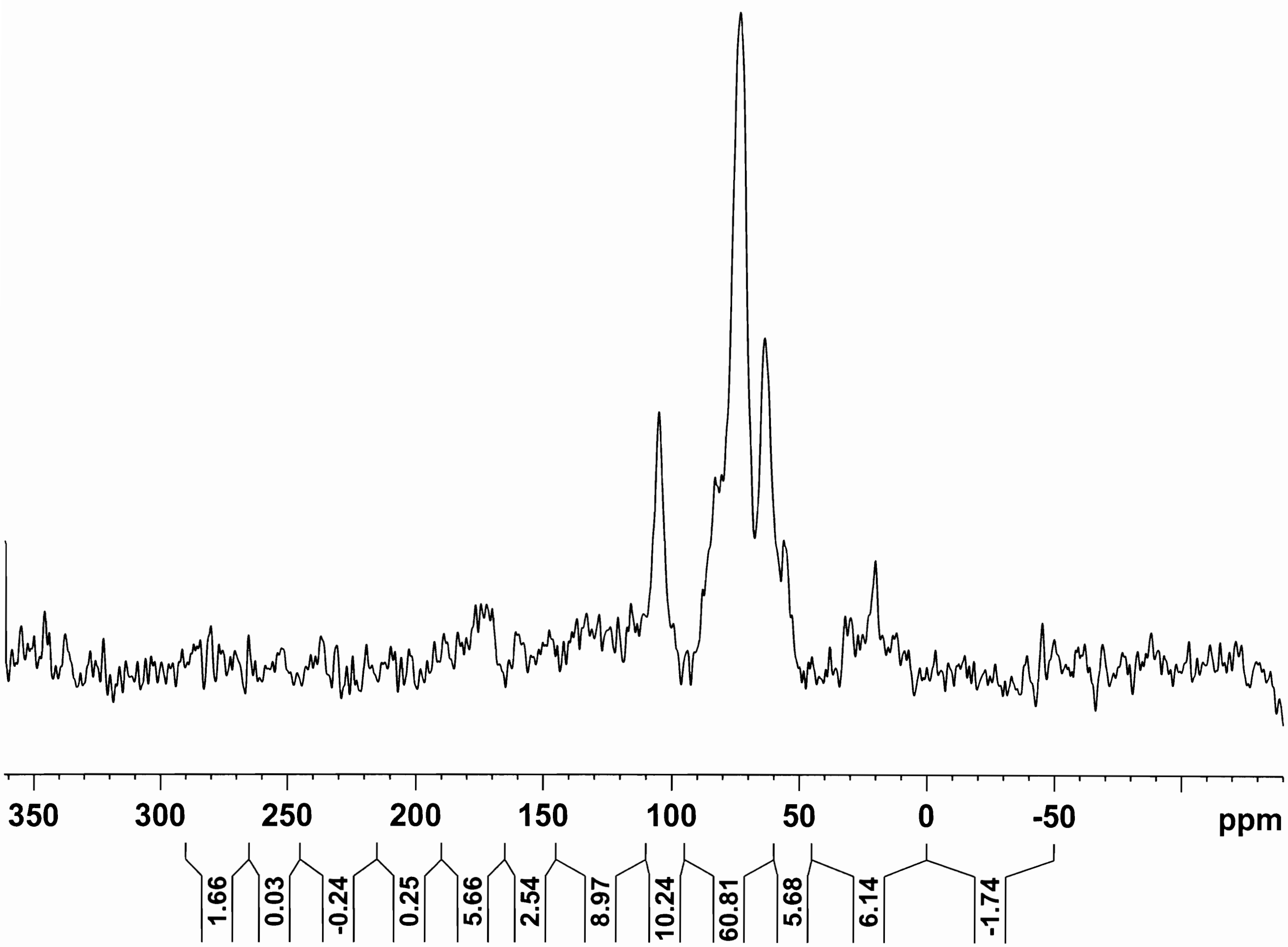
F2 - Acquisition Parameters
Date_ 20080309
Time 21.36
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 694.6 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.94 usec
PL1 1.90 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229682 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/15/2008   52.3 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters
NAME KBSNRate_LS105_7A
EXPNO 3
PROCNO 2

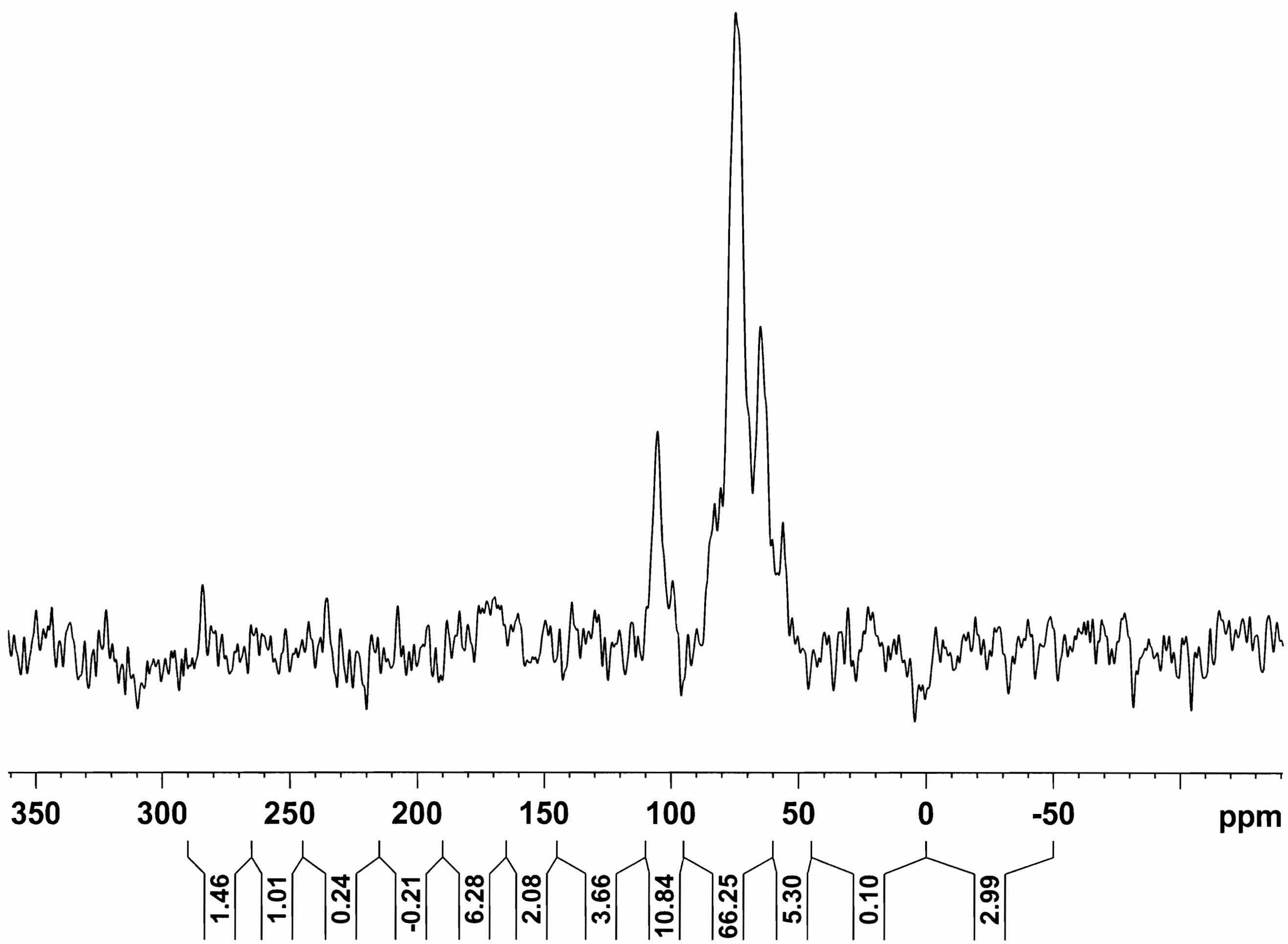
F2 - Acquisition Parameters
Date_ 20080215
Time 15.35
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG hpdec
TD 1024
SOLVENT
NS 12288
DS 2
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 14596.5
DW 19.800 usec
DE 20.00 usec
TE 698.2 K
D1 3.00000000 sec
TD0 24

======== CHANNEL f1 ========
NUC1 13C
P1 0.95 usec
PL1 1.40 dB
SFO1 50.3285161 MHz

======== CHANNEL f2 ========
NUC2 1H
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229361 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/15/2008 52.9 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



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Current Data Parameters

NAME	KBSNRate_LS101_1B
EXPNO	3
PROCNO	2

F2 - Acquisition Parameters

Date_	20080315
Time	6.29
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	2048
DW	19.800 usec
DE	6.00 usec
TE	696.2 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

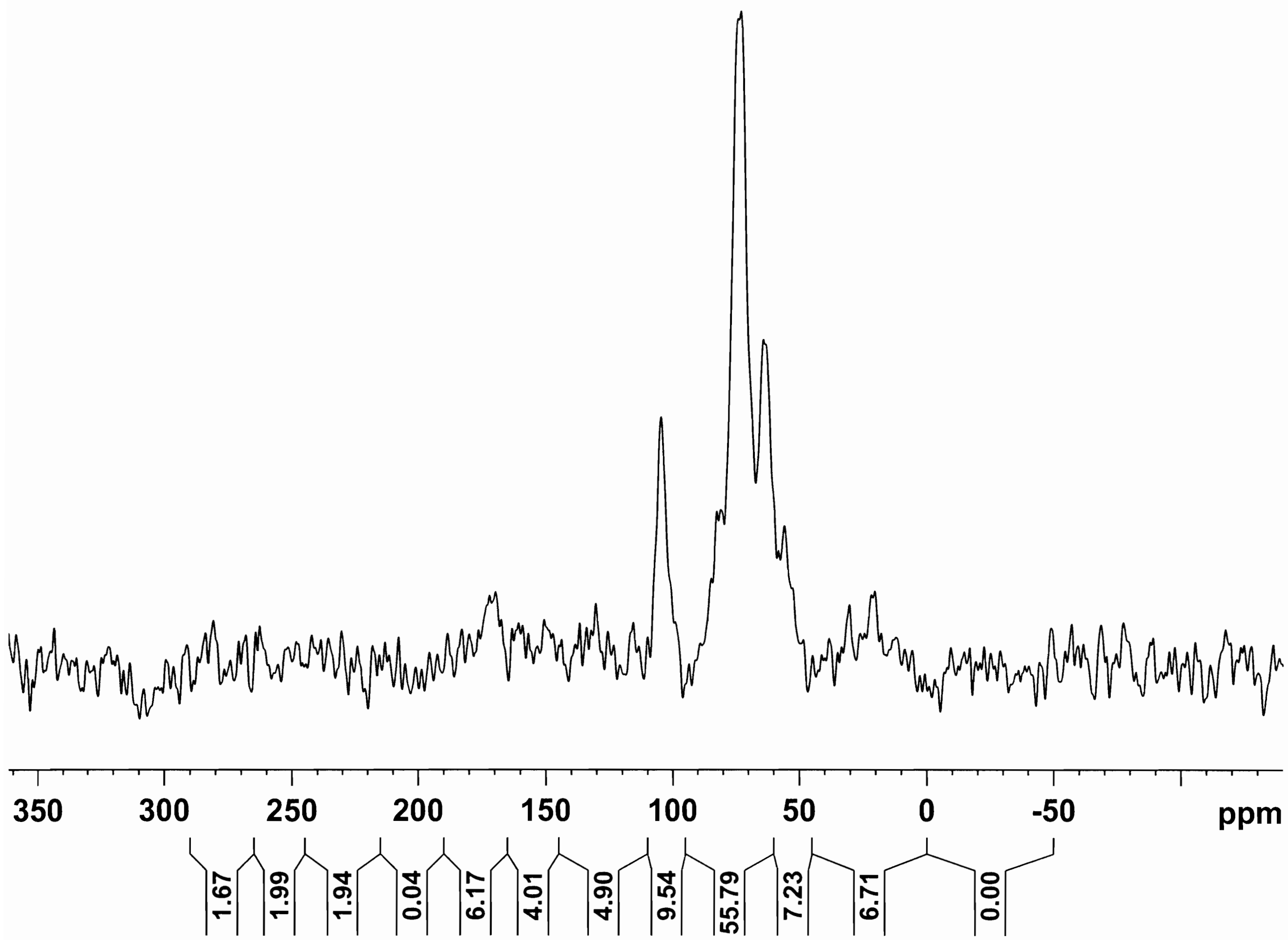
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

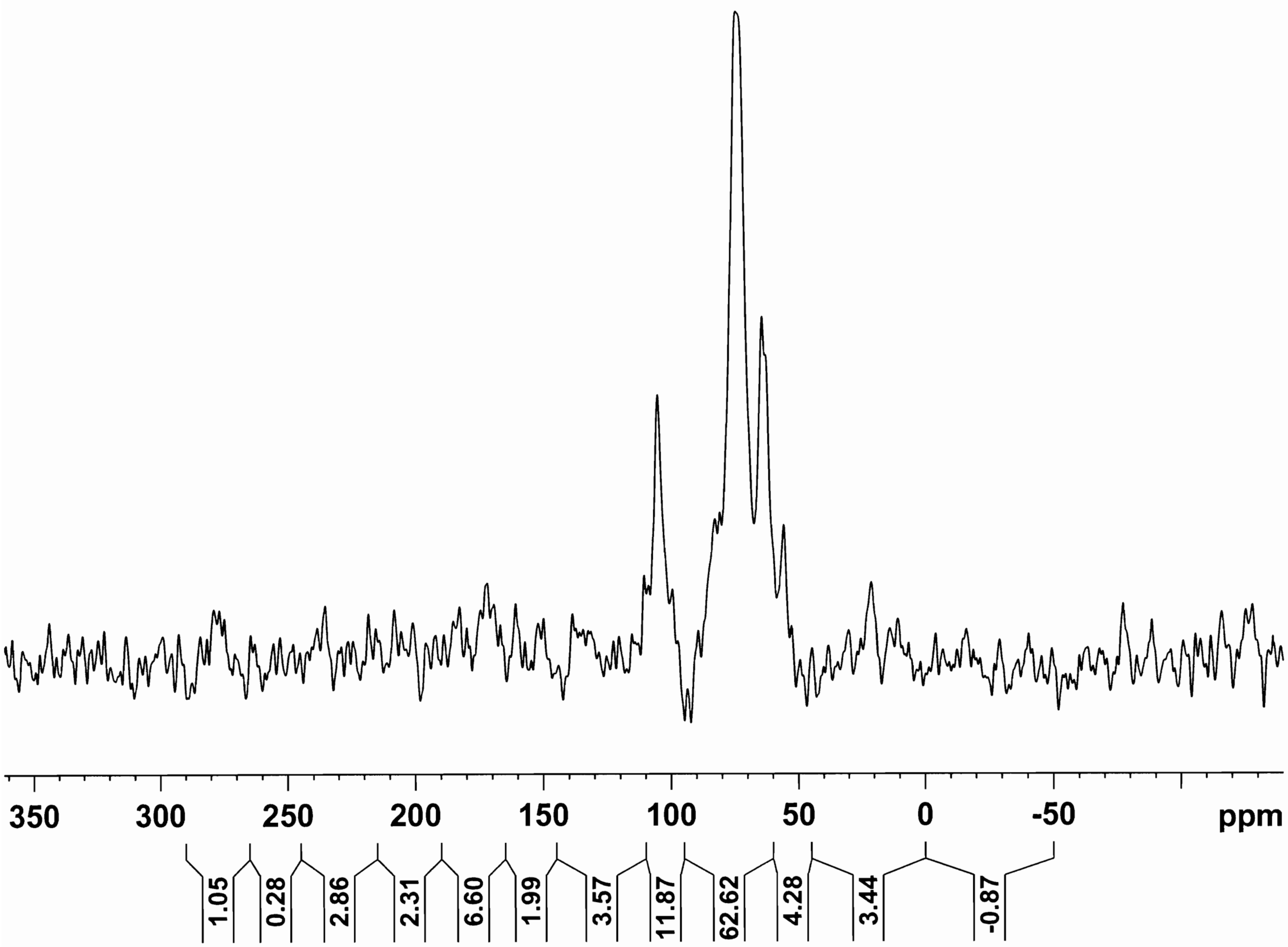
SI	16384
SF	50.3229682 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
06/28/2008   63.6 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



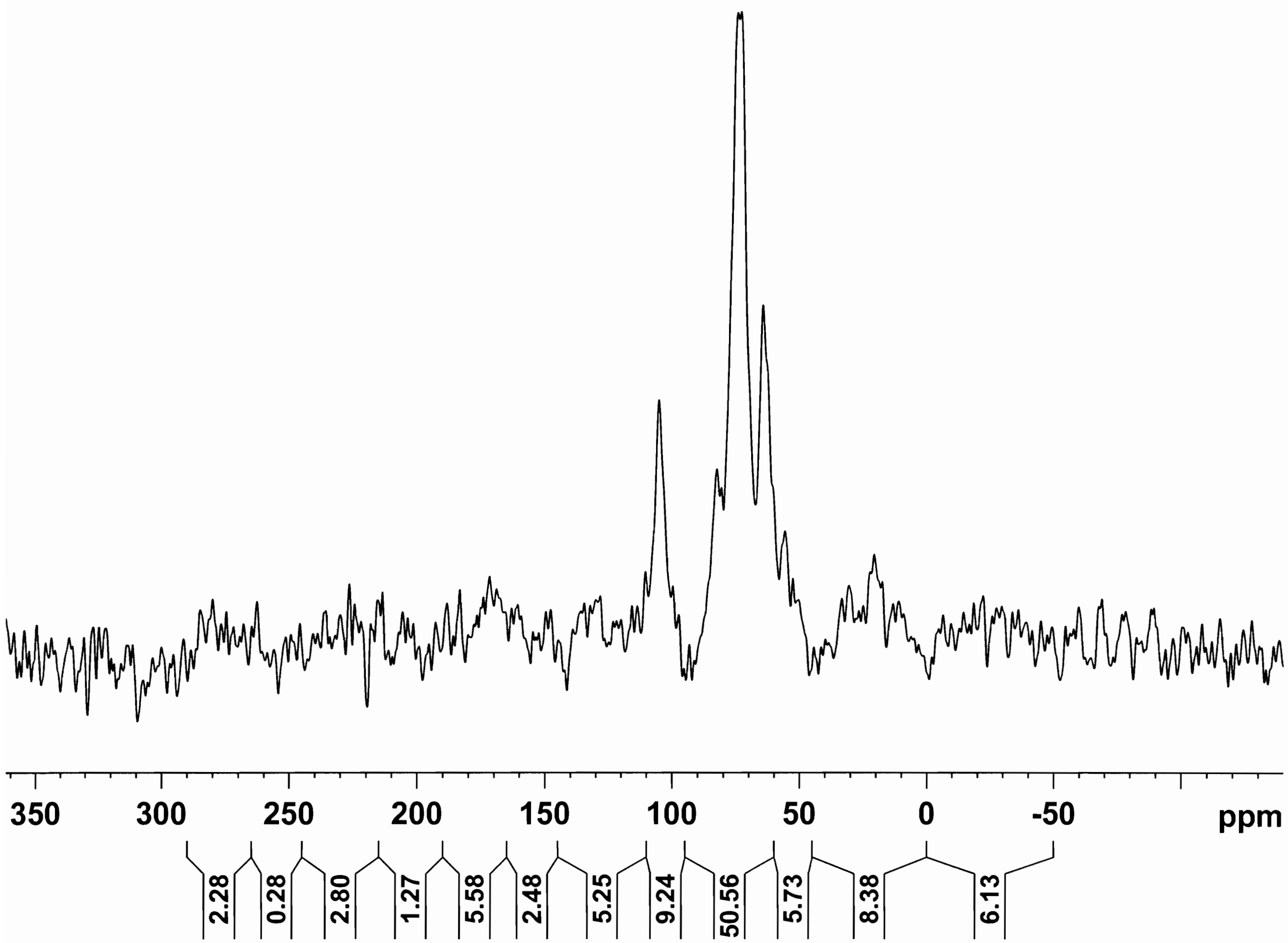

```
Current Data Parameters
NAME      KBSNRate_LS107_2B
EXPNO                     3
PROCNO                    2

F2 - Acquisition Parameters
Date_              20080628
Time                  23.48
INSTRUM               spect
PROBHD   4 mm MASxvt BB
PULPROG               hpdec
TD                     1024
SOLVENT
NS                    12288
DS                        2
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                     4096
DW                   19.800 usec
DE                     6.00 usec
TE                    697.0 K
D1               3.00000000 sec
TD0                      24

======== CHANNEL f1 ========
NUC1                    13C
P1                     0.94 usec
PL1                    1.90 dB
SFO1             50.3285161 MHz

======== CHANNEL f2 ========
NUC2                     1H
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229324 MHz
WDW                      EM
SSB                       0
LB                    50.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/24/2008   55.1 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.




```
Current Data Parameters
NAME     KBSNRate_LS106_3B
EXPNO                    3
PROCNO                   3

F2 - Acquisition Parameters
Date_           20080625
Time                1.25
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG            hpdec
TD                  1024
SOLVENT
NS                 12288
DS                     2
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                  4096
DW                19.800 usec
DE                  6.00 usec
TE                 695.9 K
D1            3.00000000 sec
TD0                   24

======== CHANNEL f1 ========
NUC1                 13C
P1                  0.94 usec
PL1                 1.90 dB
SFO1          50.3285161 MHz

======== CHANNEL f2 ========
NUC2                  1H
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3229324 MHz
WDW                   EM
SSB                    0
LB                 50.00 Hz
GB                     0
PC                  1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/25/2008   52.8 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_LS102_4B
EXPNO	3
PROCNO	2

F2 - Acquisition Parameters

Date_	20080625
Time	21.29
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	2
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	4096
DW	19.800 usec
DE	6.00 usec
TE	696.0 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

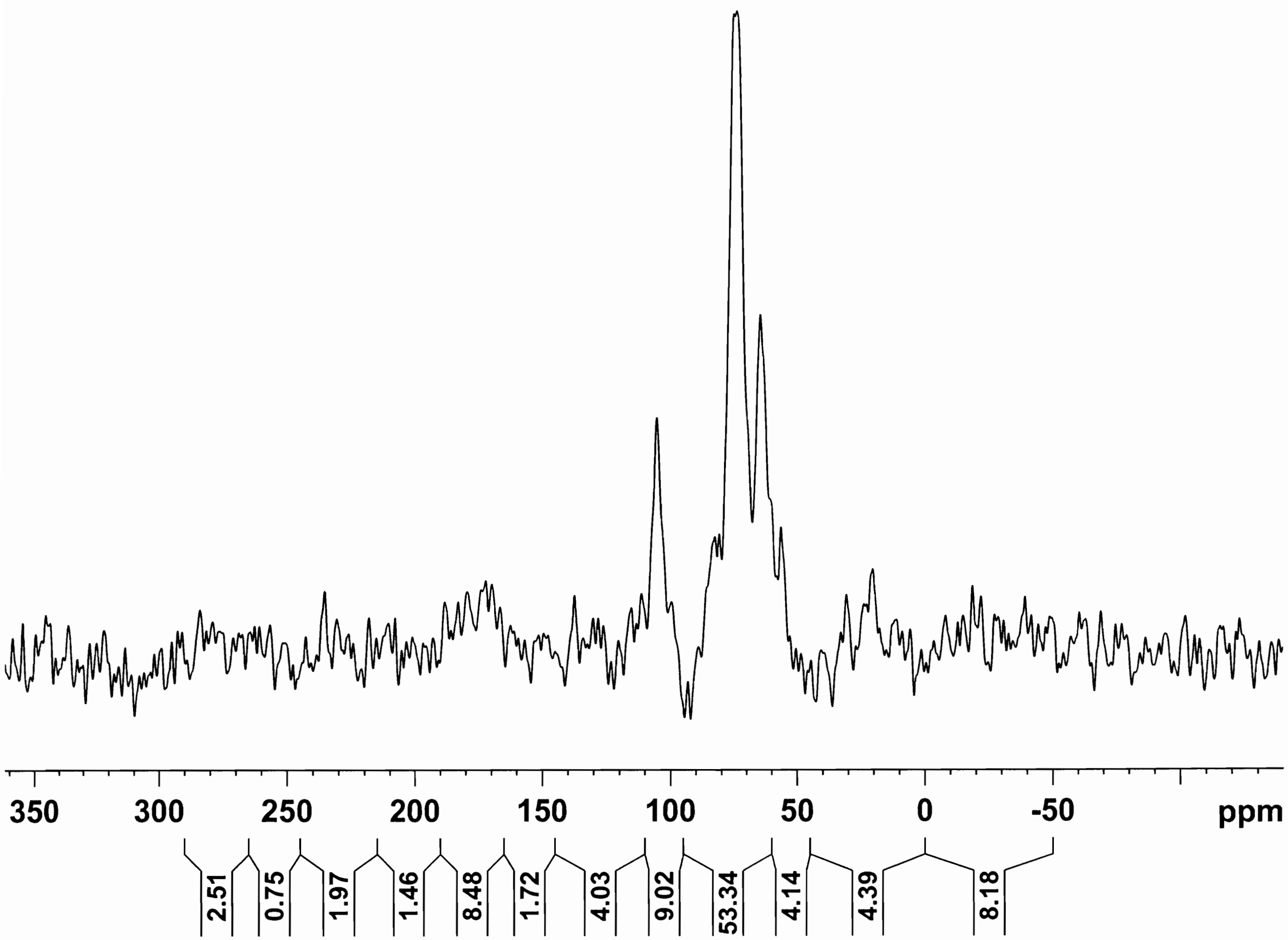
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229324 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/26/2008   51.4 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



Current Data Parameters

NAME	KBSNRate_LS104_5B
EXPNO	3
PROCNO	3

F2 - Acquisition Parameters

Date_	20080626
Time	21.36
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	hpdec
TD	1024
SOLVENT	
NS	12288
DS	2
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	4096
DW	19.800 usec
DE	6.00 usec
TE	695.8 K
D1	3.00000000 sec
TD0	24

======== CHANNEL f1 ========

NUC1	13C
P1	0.94 usec
PL1	1.90 dB
SFO1	50.3285161 MHz

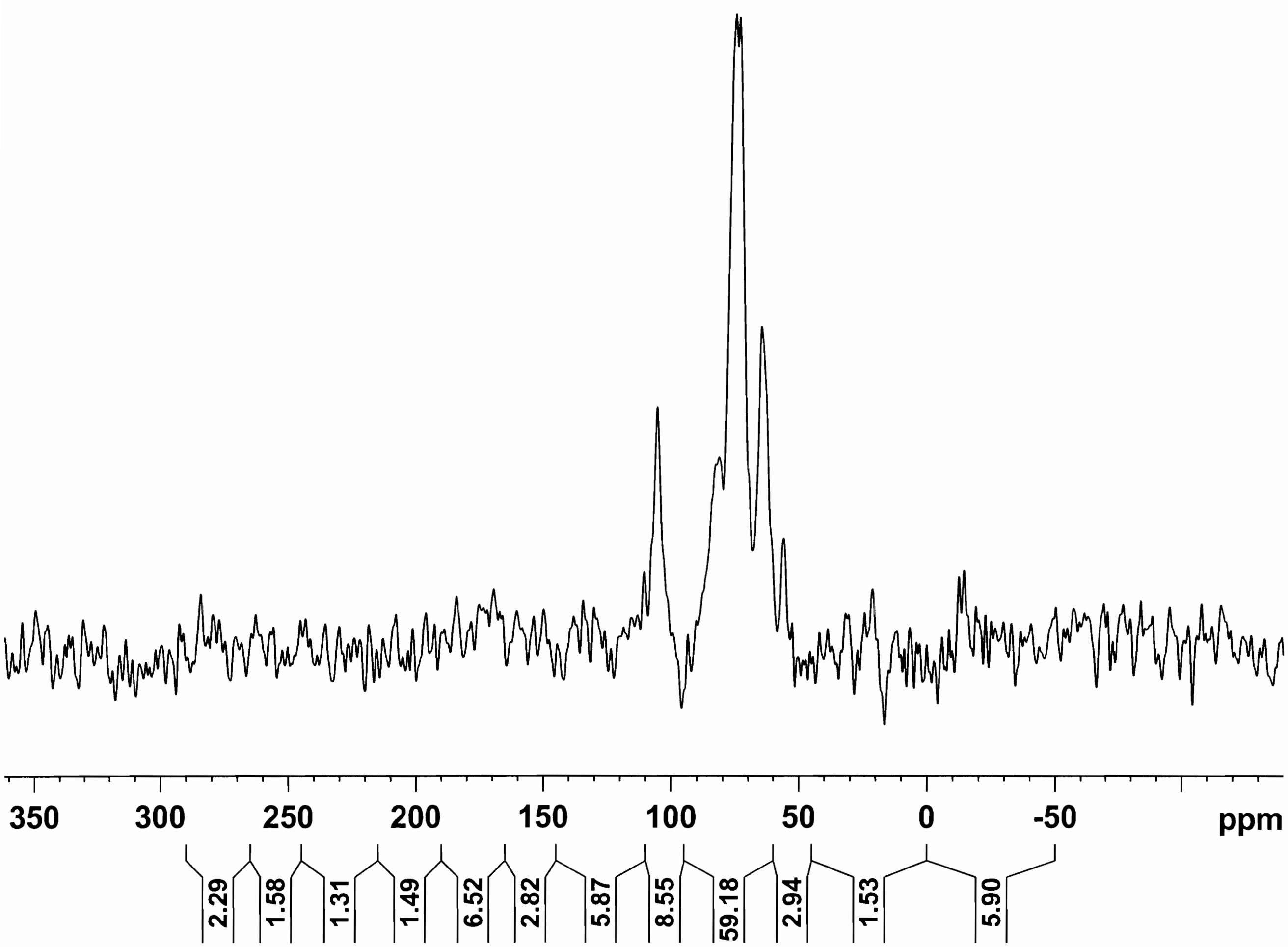
======== CHANNEL f2 ========

NUC2	1H
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

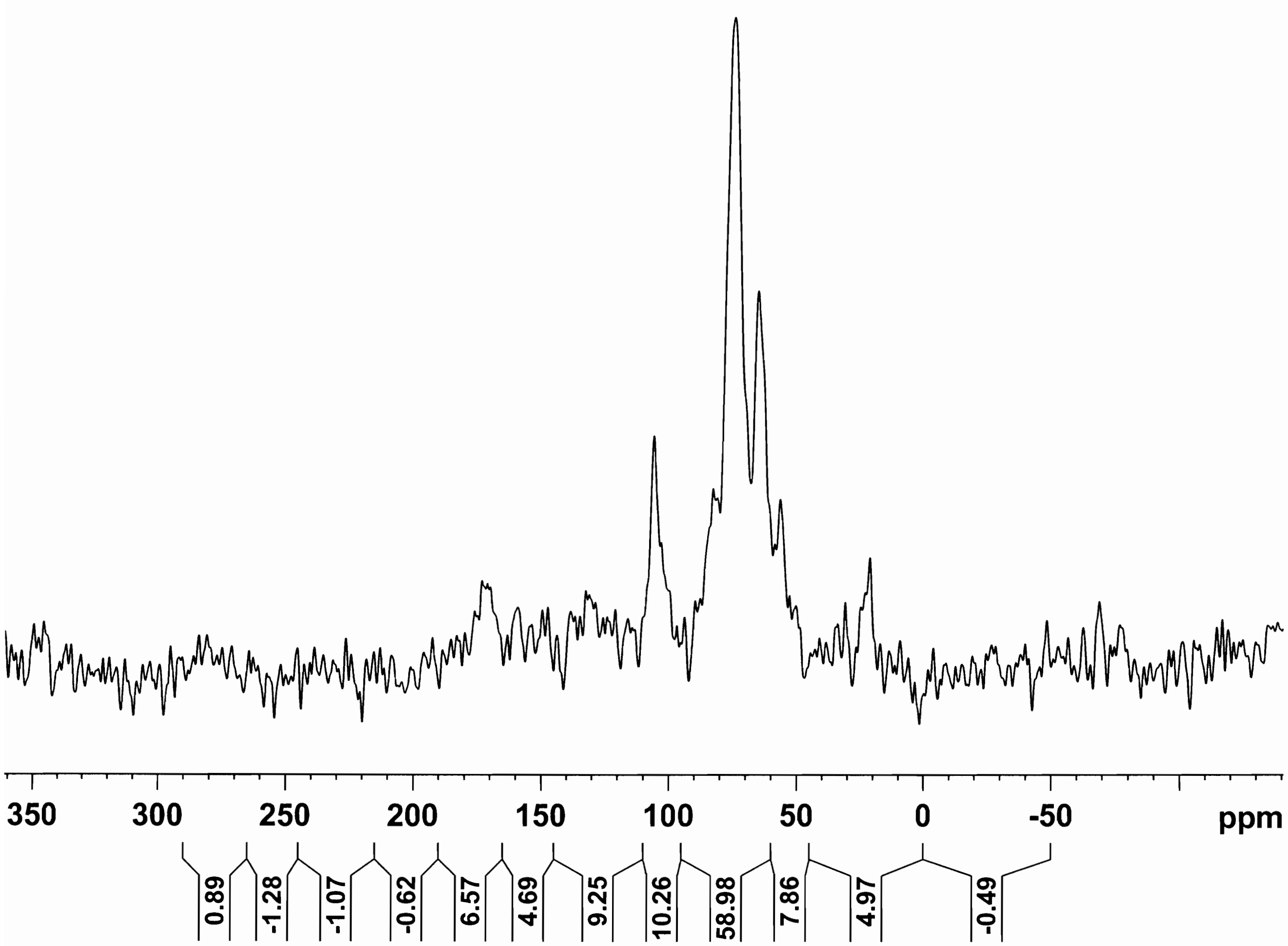
SI	16384
SF	50.3229324 MHz
WDW	EM
SSB	0
LB	50.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/27/2008   56.5 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.




```
Current Data Parameters
NAME      KBSNRate_LS103_6B
EXPNO                     3
PROCNO                    2

F2 - Acquisition Parameters
Date_              20080627
Time                  21.15
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG               hpdec
TD                     1024
SOLVENT
NS                    12288
DS                        2
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                     4096
DW                   19.800 usec
DE                     6.00 usec
TE                    697.0 K
D1               3.00000000 sec
TD0                      24

======== CHANNEL f1 ========
NUC1                    13C
P1                     0.94 usec
PL1                    1.90 dB
SFO1            50.3285161 MHz

======== CHANNEL f2 ========
NUC2                     1H
PL2                    6.00 dB
PL12                   3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229324 MHz
WDW                      EM
SSB                       0
LB                    50.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/15/2008 52.5 mg
4mm MAS probe. 5 kHz. Bloch decay 20 deg w background subtraction.



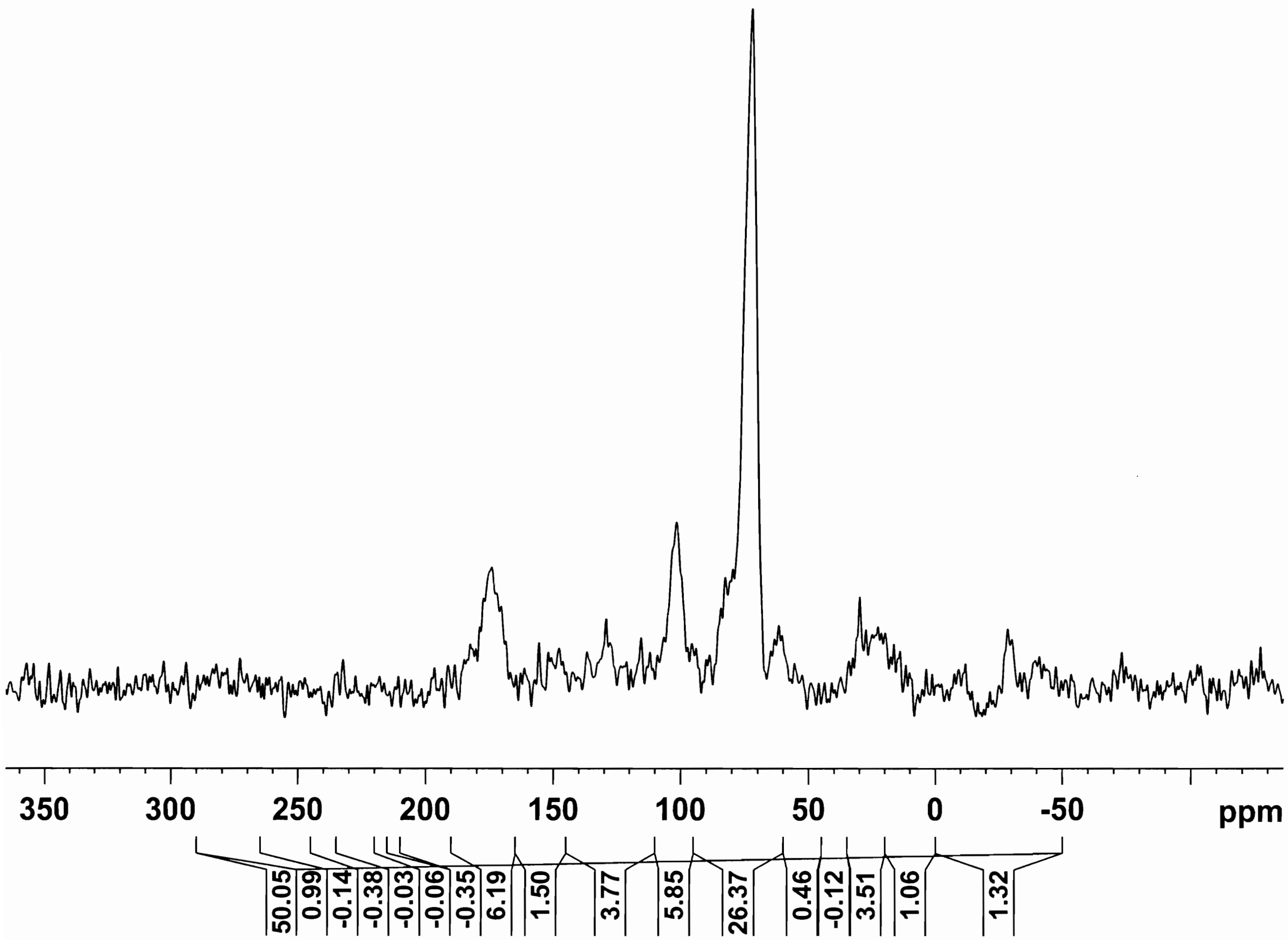

```
Current Data Parameters
NAME      KBSNRate_LS105_7B
EXPNO                     3
PROCNO                    3

F2 - Acquisition Parameters
Date_              20080315
Time                  21.56
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG               hpdec
TD                     1024
SOLVENT
NS                    12288
DS                        0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                     2048
DW                   19.800 usec
DE                     6.00 usec
TE                    696.4 K
D1               3.00000000 sec
TD0                      24

======== CHANNEL f1 ========
NUC1                    13C
P1                     0.94 usec
PL1                    1.90 dB
SFO1             50.3285161 MHz

======== CHANNEL f2 ========
NUC2                     1H
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229682 MHz
WDW                      EM
SSB                       0
LB                    50.00 Hz
GB                        0
PC                     1.00
```

APPENDIX F

^{13}C NMR Dipolar Dephasing Spectra

Solid-state ^{13}C NMR was performed at Rice University using Bruker 200 MHz NMR spectrometer. C-13 NMR dipolar dephasing-magic angle spinning spectra were collected for grain and leaf and stem samples from the N Rate Experiment (Figure F1).

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Grain, Treatment 0 kg N/ha, Replicate 1, Cover Crop
02/16/2008 109.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain101_1A
EXPNO 2
PROCNO 1

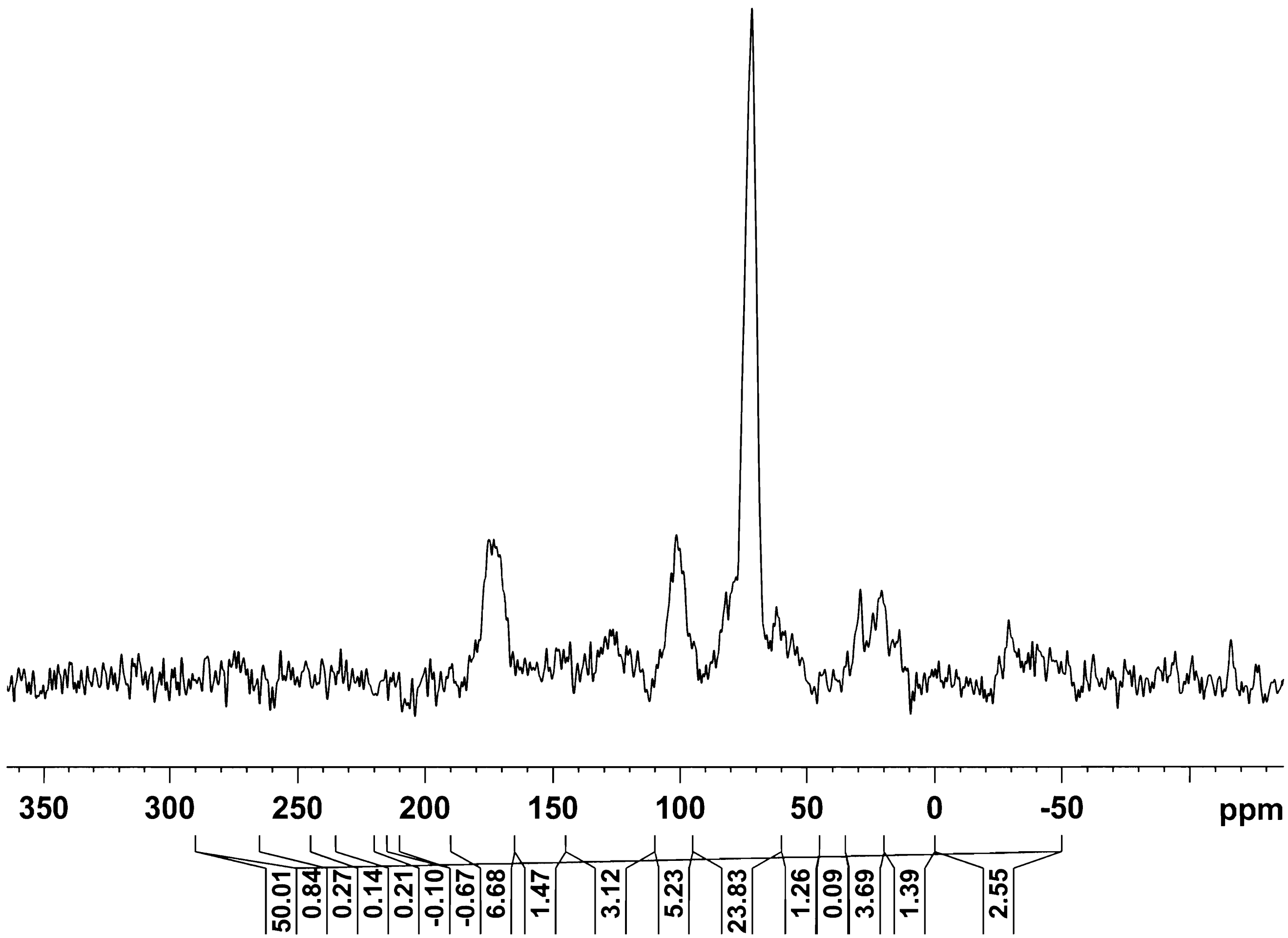
F2 - Acquisition Parameters
Date_ 20080216
Time 3.18
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 3649.1
DW 19.800 usec
DE 6.00 usec
TE 698.4 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.00 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

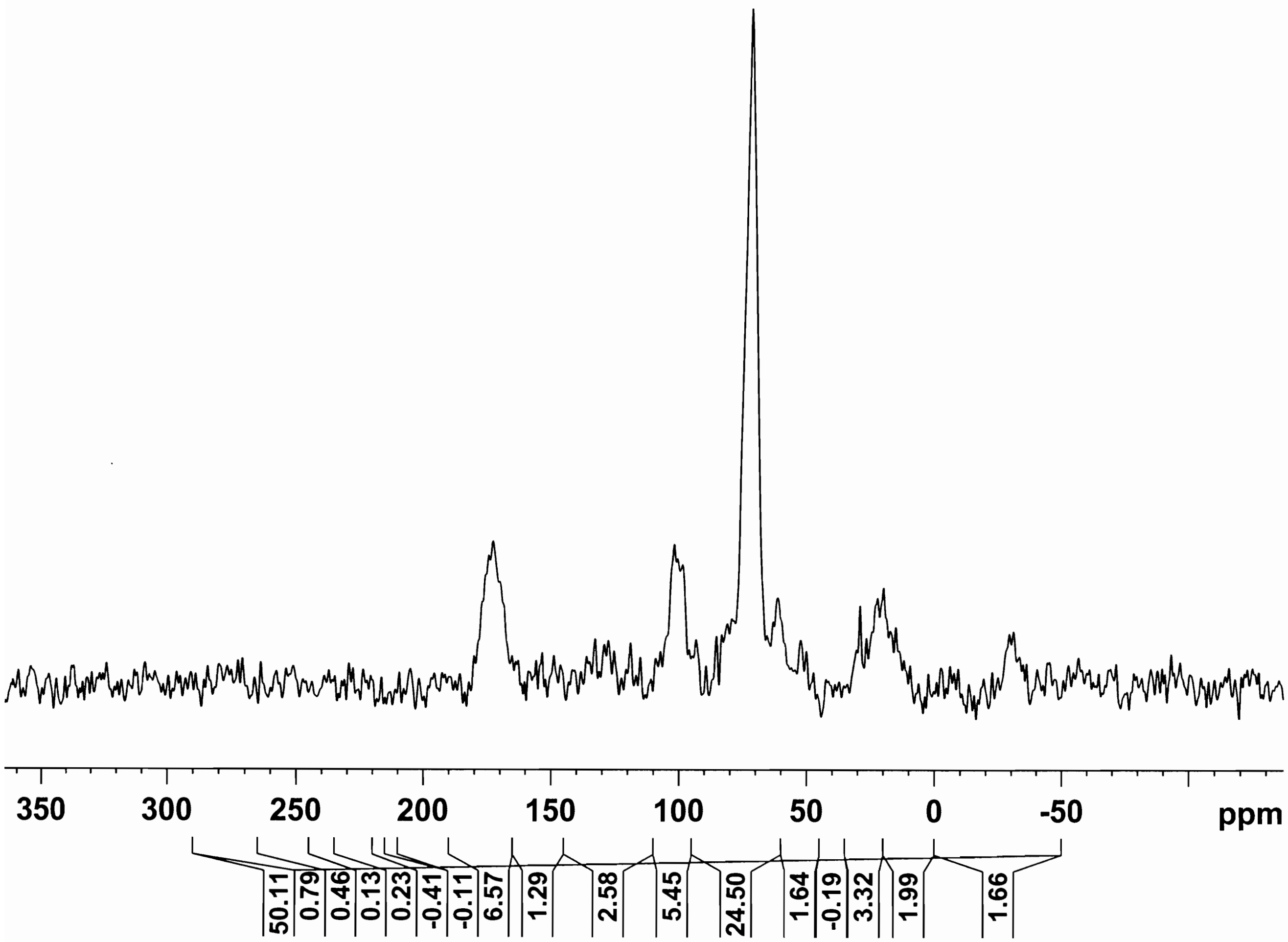
F2 - Processing parameters
SI 16384
SF 50.3229351 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Grain, Treatment 34 kg N/ha, Replicate 1, Cover Crop
03/04/2008 103.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



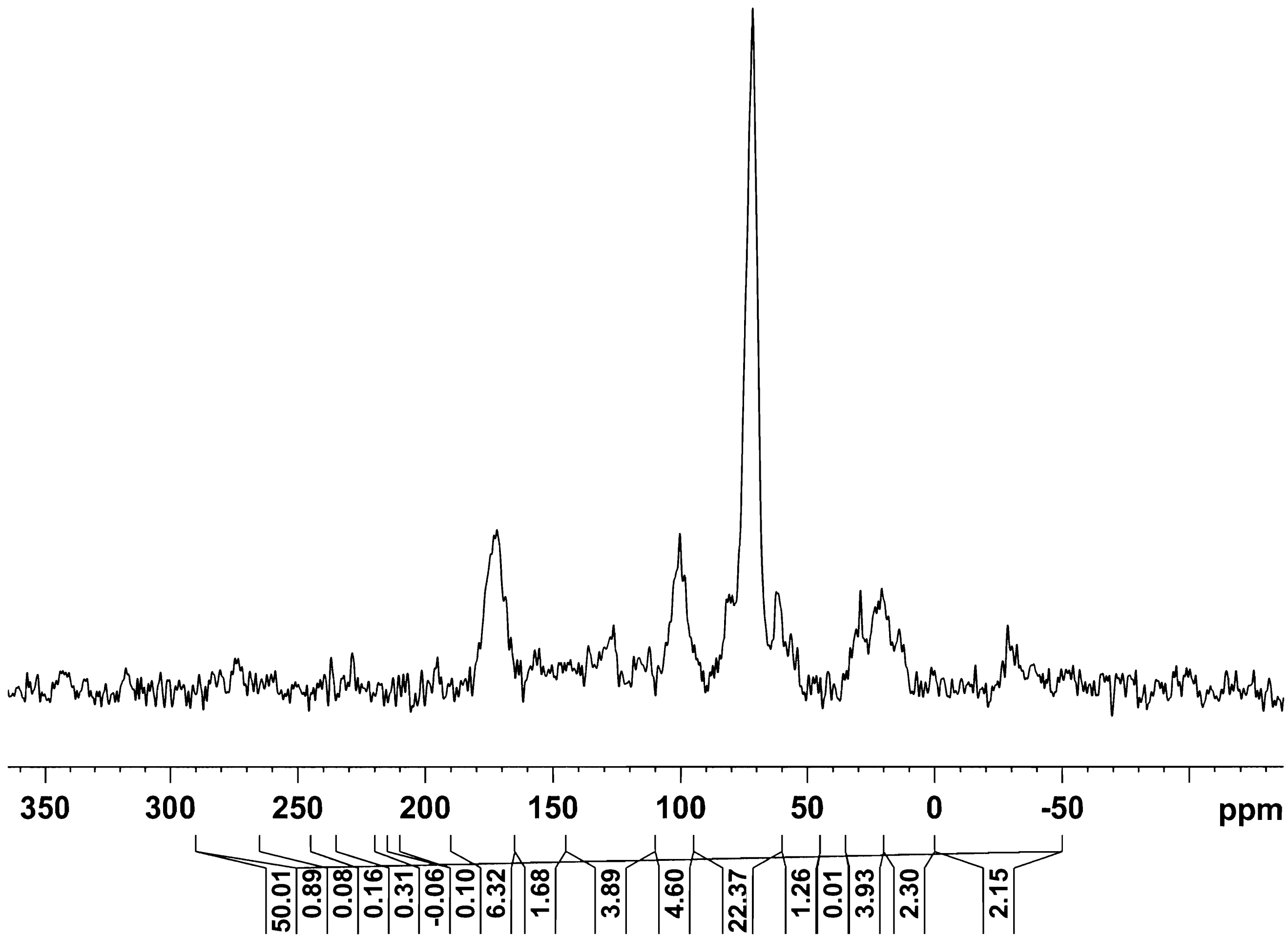
Current Data Parameters		
NAME	KBSNRate_Grain107_2A	
EXPNO	2	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20080304	
Time	12.53	
INSTRUM	spect	
PROBHD	4 mm MASxvt BB	
PULPROG	cpnqs.99.LBA	
TD	1024	
SOLVENT		
NS	3500	
DS	0	
SWH	25252.525	Hz
FIDRES	24.660669	Hz
AQ	0.0203450	sec
RG	2580.3	
DW	19.800	usec
DE	6.00	usec
TE	698.0	K
D1	2.00000000	sec
D3	0.00002500	sec
======== CHANNEL f1 ========		
NUC1	13C	
P2	8.60	usec
P15	1000.00	usec
PL1	1.40	dB
PL11	1.90	dB
SFO1	50.3287071	MHz
======== CHANNEL f2 ========		
CPDPRG2	tppm15	
NUC2	1H	
P3	3.05	usec
P31	5.10	usec
PL2	6.00	dB
PL12	3.00	dB
SFO2	200.1315000	MHz
F2 - Processing parameters		
SI	16384	
SF	50.3229663	MHz
WDW	EM	
SSB	0	
LB	30.00	Hz
GB	0	
PC	1.00	

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Grain, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/05/2008   103.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



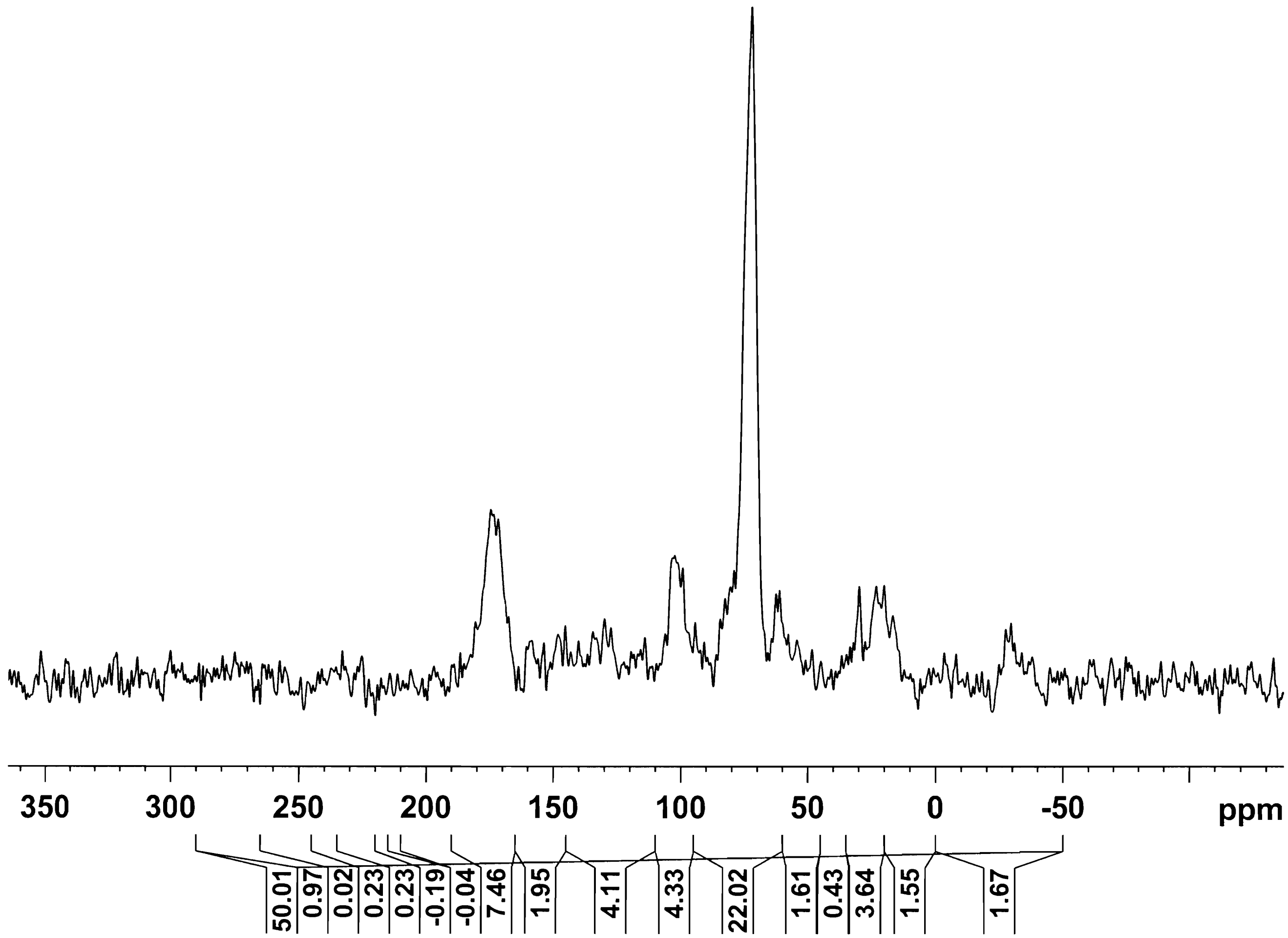

```
Current Data Parameters
NAME      KBSNRate_Grain106_3A
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080305
Time                  4.17
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG     cpnqs.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                2580.3
DW                19.800 usec
DE                  6.00 usec
TE                 697.8 K
D1            2.00000000 sec
D3            0.00002500 sec

======== CHANNEL f1 ========
NUC1                   13C
P2                    8.60 usec
P15                1000.00 usec
PL1                   1.40 dB
PL11                  1.90 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.05 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229663 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Grain, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/05/2008   111.2mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



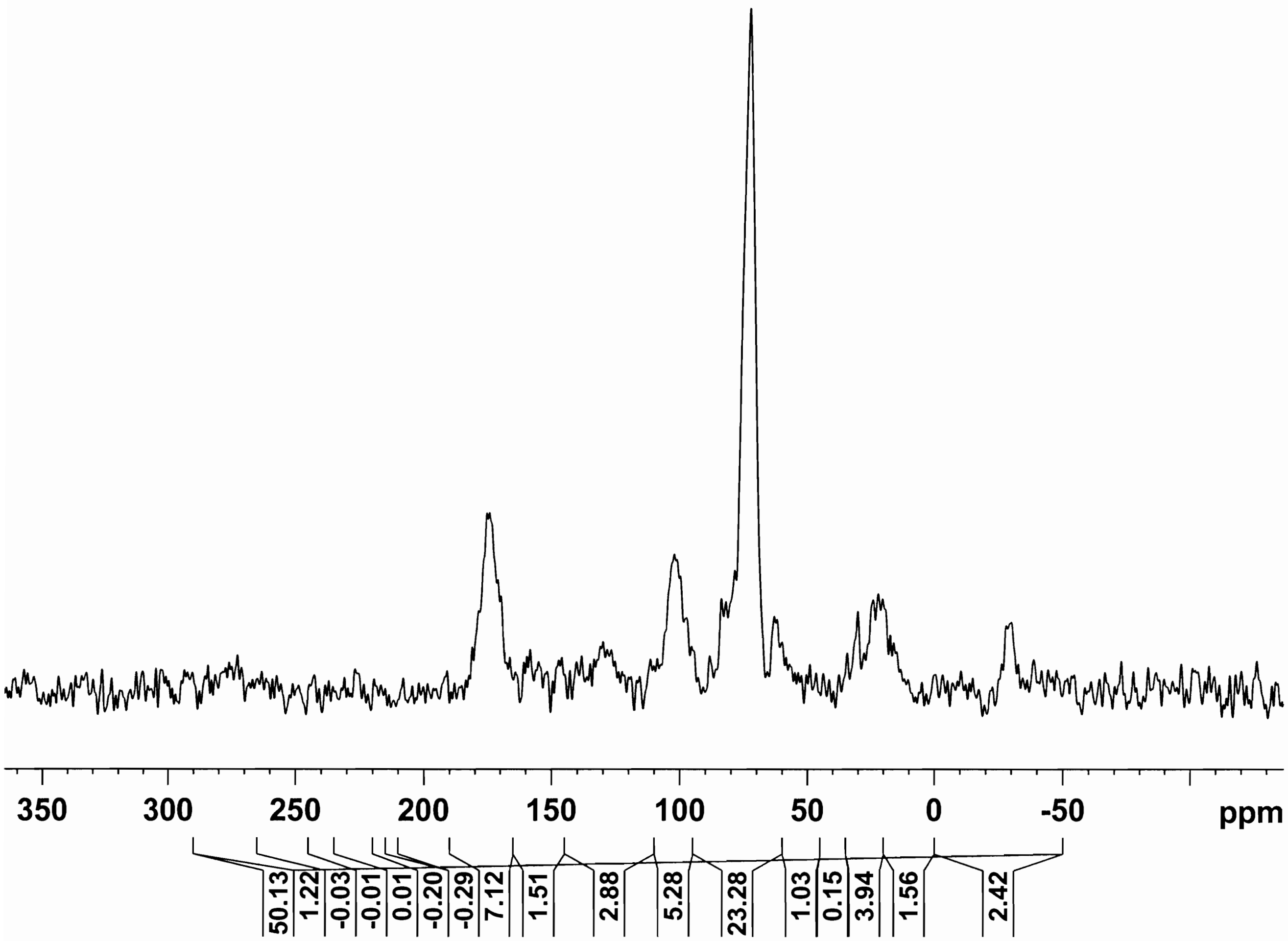

```
Current Data Parameters
NAME     KBSNRate_Grain102_4A
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_            20080305
Time                21.02
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG    cpnqs.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                 4597.6
DW                 19.800 usec
DE                   6.00 usec
TE                  698.0 K
D1             2.00000000 sec
D3             0.00002500 sec

======== CHANNEL f1 ========
NUC1                  13C
P2                   8.60 usec
P15               1000.00 usec
PL1                  1.40 dB
PL11                 1.90 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.05 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229663 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Grain, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/06/2008   103.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME     KBSNRate_Grain104_5A
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20080306
Time               15.28
INSTRUM            spect
PROBHD   4 mm MASxvt BB
PULPROG    cpnqs.99.LBA
TD                  1024
SOLVENT
NS                  3500
DS                     0
SWH            25252.525 Hz
FIDRES         24.660669 Hz
AQ             0.0203450 sec
RG                4597.6
DW                19.800 usec
DE                  6.00 usec
TE                 695.0 K
D1            2.00000000 sec
D3            0.00002500 sec

======== CHANNEL f1 ========
NUC1                 13C
P2                  8.60 usec
P15              1000.00 usec
PL1                 1.40 dB
PL11                1.90 dB
SFO1          50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2           tppm15
NUC2                  1H
P3                  3.05 usec
P31                 5.10 usec
PL2                 6.00 dB
PL12                3.00 dB
SFO2         200.1315000 MHz

F2 - Processing parameters
SI                 16384
SF            50.3229663 MHz
WDW                   EM
SSB                    0
LB                 30.00 Hz
GB                     0
PC                  1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Grain, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/07/2008   102.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME   KBSNRate_Grain103_6A
EXPNO   2
PROCNO   1

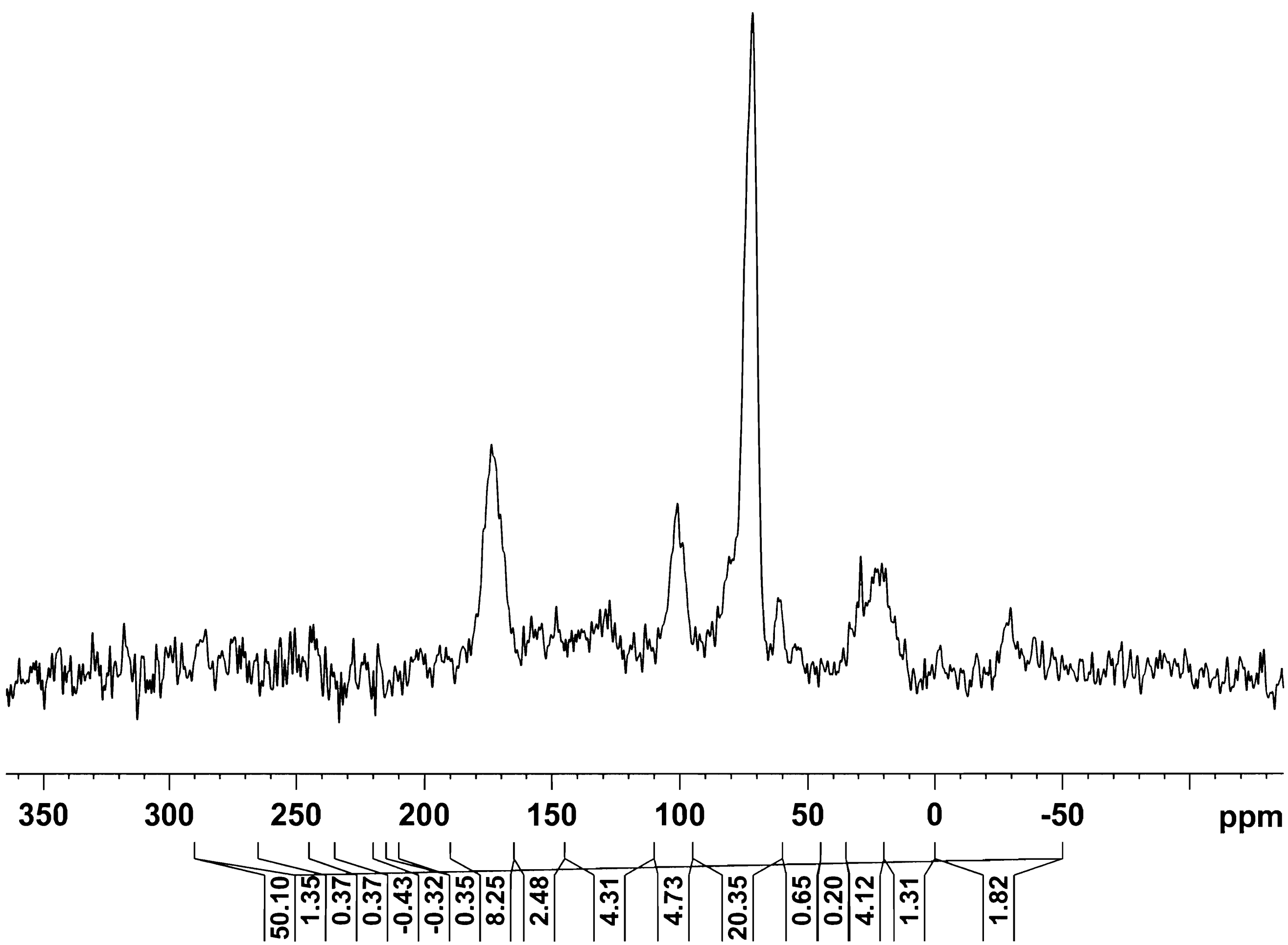
F2 - Acquisition Parameters
Date_   20080307
Time   6.44
INSTRUM   spect
PROBHD   4 mm MASxvt BB
PULPROG   cpnqs.99.LBA
TD   1024
SOLVENT
NS   3500
DS   0
SWH   25252.525 Hz
FIDRES   24.660669 Hz
AQ   0.0203450 sec
RG   4597.6
DW   19.800 usec
DE   6.00 usec
TE   694.2 K
D1   2.00000000 sec
D3   0.00002500 sec

======== CHANNEL f1 ========
NUC1   13C
P2   8.60 usec
P15   1000.00 usec
PL1   1.40 dB
PL11   1.90 dB
SFO1   50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2   tppm15
NUC2   1H
P3   3.05 usec
P31   5.10 usec
PL2   6.00 dB
PL12   3.00 dB
SFO2   200.1315000 MHz

F2 - Processing parameters
SI   16384
SF   50.3229663 MHz
WDW   EM
SSB   0
LB   30.00 Hz
GB   0
PC   1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Grain, Treatment 202 kg N/ha, Replicate 1, Cover Crop
03/11/2008 109.7 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain105_7A
EXPNO 3
PROCNO 1

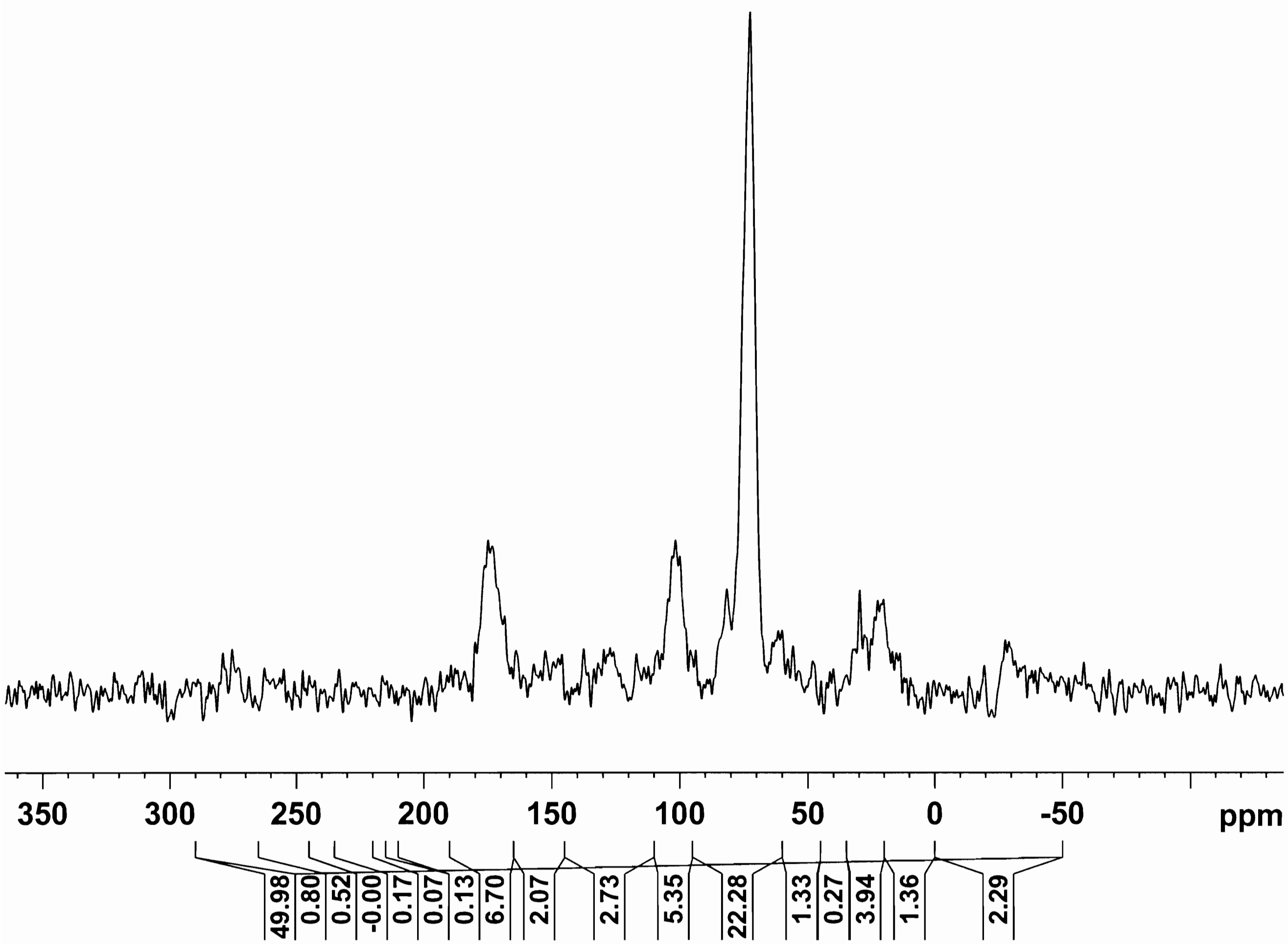
F2 - Acquisition Parameters
Date_ 20080311
Time 13.36
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2896.3
DW 19.800 usec
DE 6.00 usec
TE 694.5 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Grain, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/13/2008 103.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain101_1B
EXPNO 2
PROCNO 1

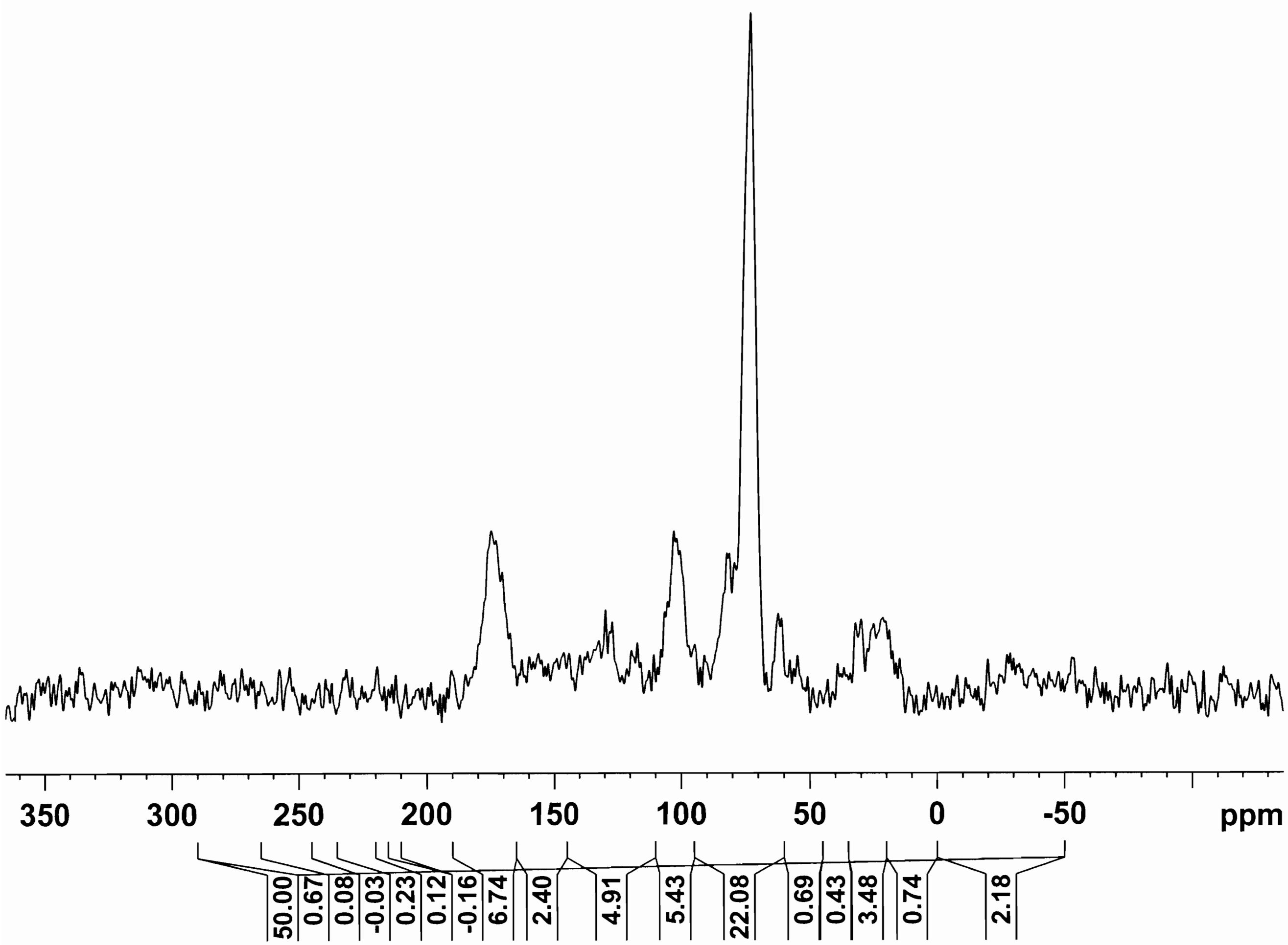
F2 - Acquisition Parameters
Date_ 20080313
Time 21.28
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2048
DW 19.800 usec
DE 6.00 usec
TE 698.0 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Grain, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
06/29/2008   102.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain107_2B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_	20080629
Time	10.48
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cpnqs.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	1625.5
DW	19.800 usec
DE	6.00 usec
TE	697.0 K
D1	2.00000000 sec
D3	0.00002500 sec

======== CHANNEL f1 ========

NUC1	13C
P2	8.60 usec
P15	1000.00 usec
PL1	1.40 dB
PL11	1.90 dB
SFO1	50.3287071 MHz

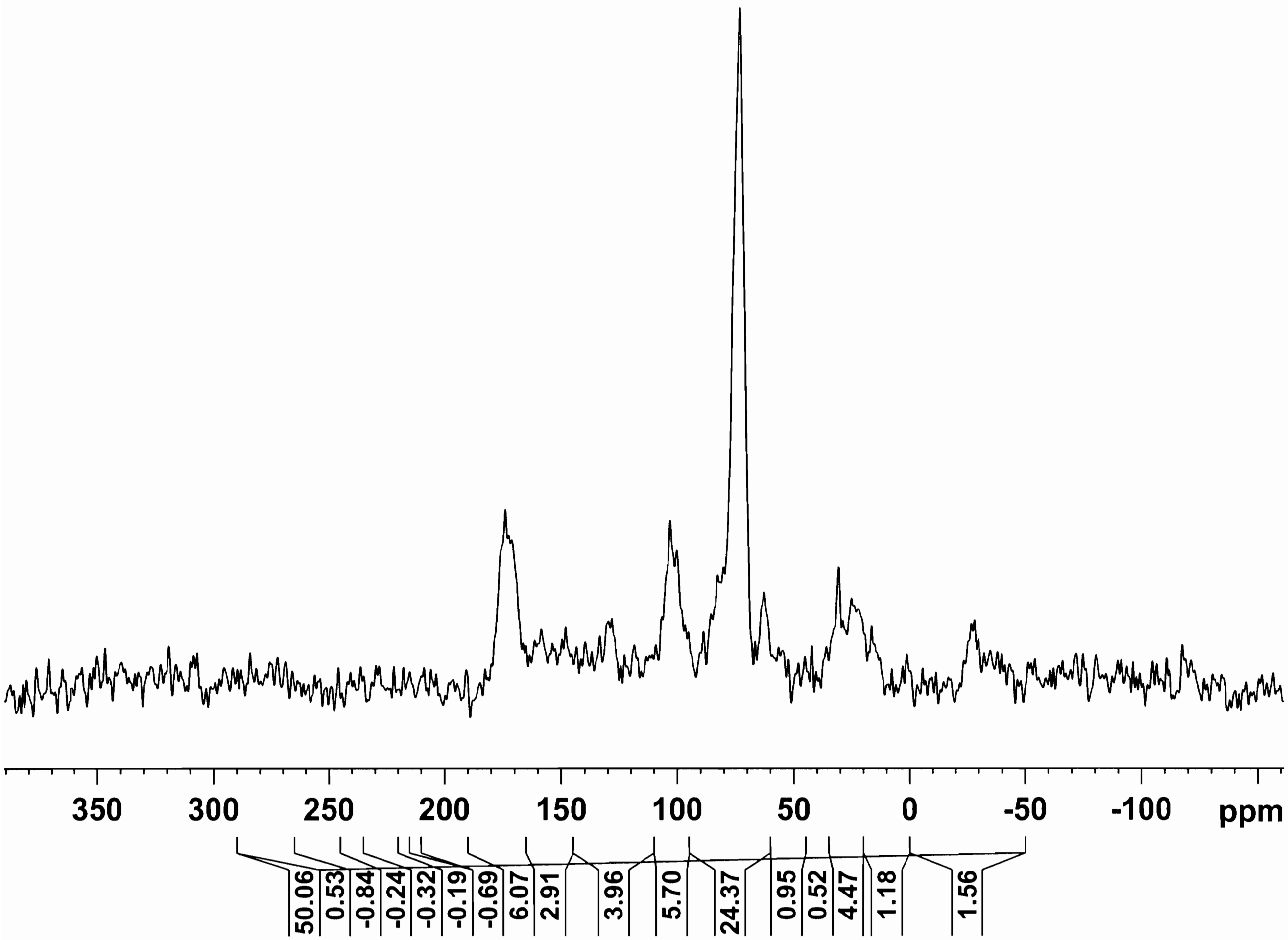
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.20 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229331 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Grain, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/16/2008   100.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain106_3B
EXPNO 2
PROCNO 1

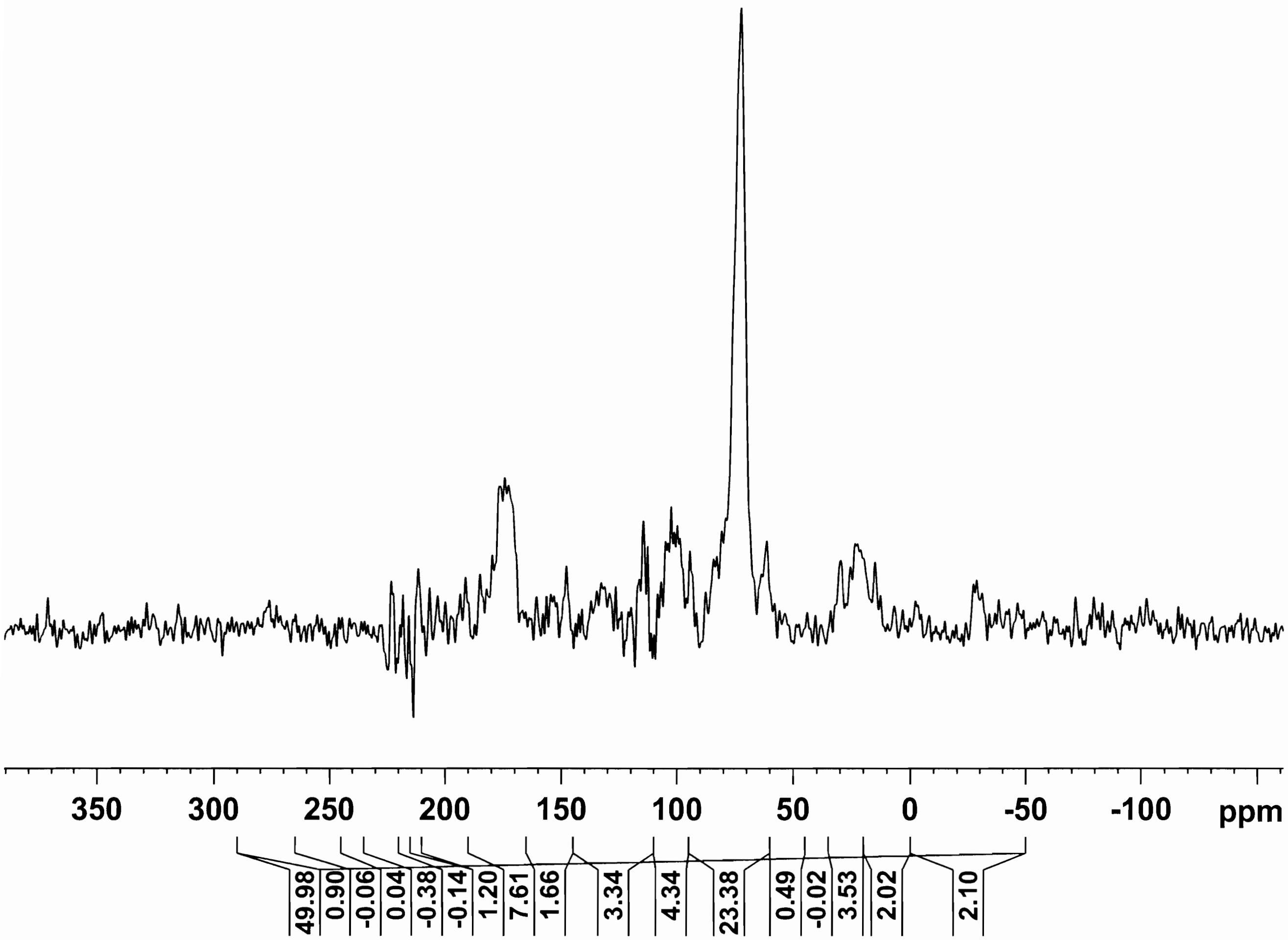
F2 - Acquisition Parameters
Date_ 20080616
Time 22.19
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 1625.5
DW 18.000 usec
DE 6.00 usec
TE 697.6 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229334 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Grain, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/14/2008 105.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_Grain102_4B
EXPNO 2
PROCNO 1

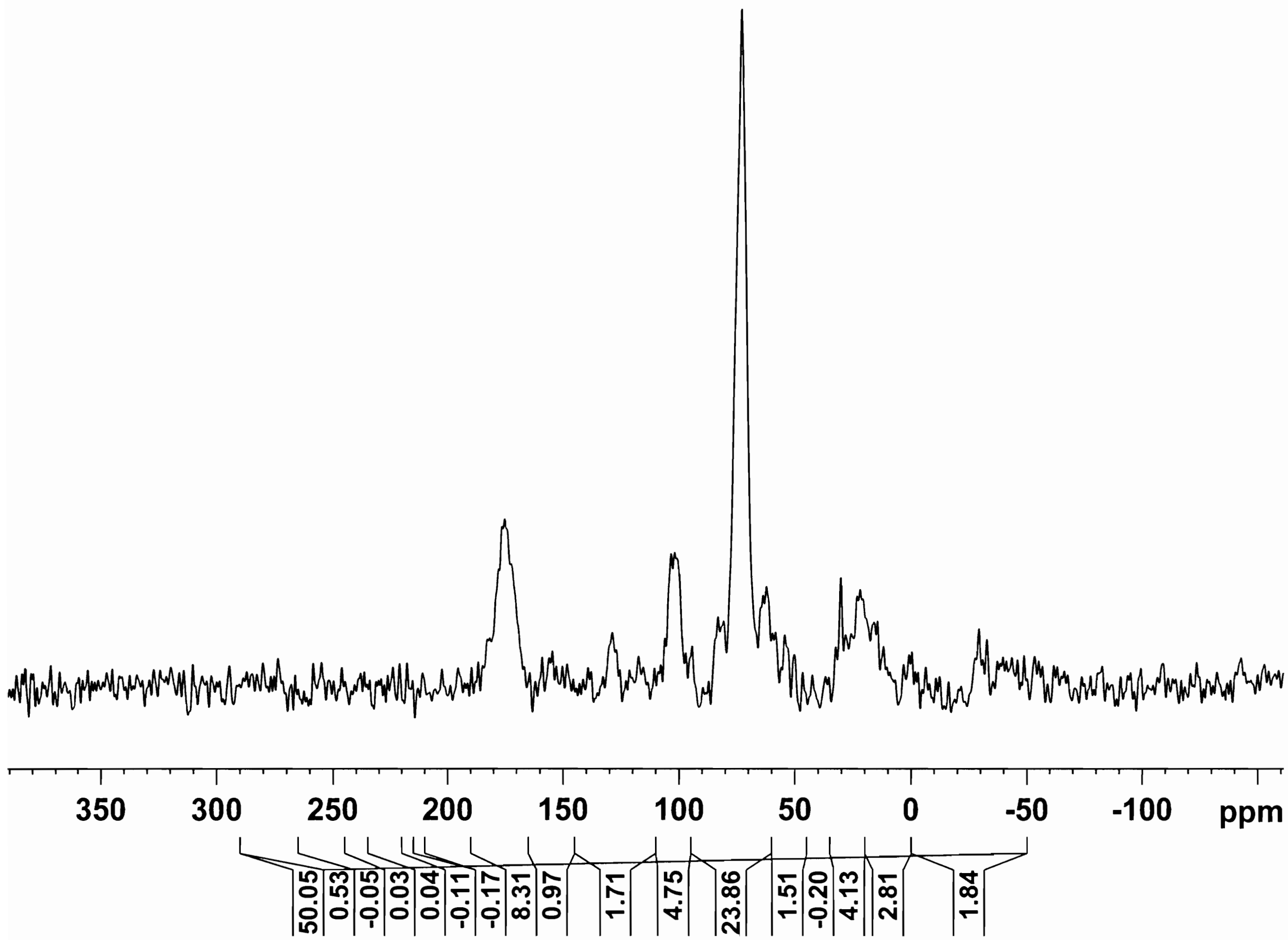
F2 - Acquisition Parameters
Date_ 20080614
Time 14.23
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 27777.777 Hz
FIDRES 27.126736 Hz
AQ 0.0185000 sec
RG 1448.2
DW 18.000 usec
DE 6.00 usec
TE 697.6 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.10 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

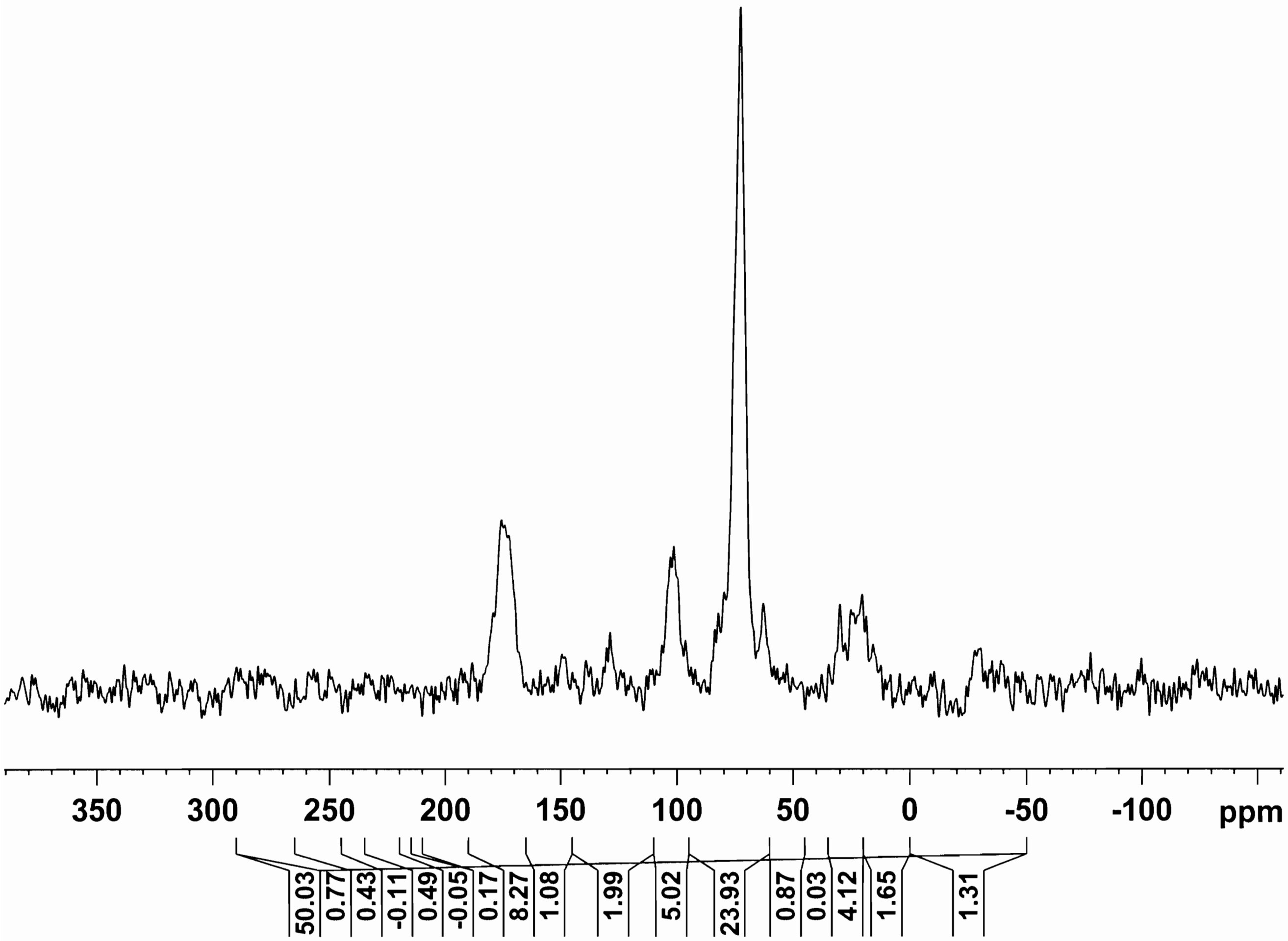
F2 - Processing parameters
SI 16384
SF 50.3229334 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Grain, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/12/2008   100.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME     KBSNRate_Grain104_5B
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080612
Time                19.43
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG    cpnqs.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             27777.777 Hz
FIDRES          27.126736 Hz
AQ              0.0185000 sec
RG                   3251
DW                 18.000 usec
DE                   6.00 usec
TE                  698.3 K
D1             2.00000000 sec
D3             0.00002500 sec

======== CHANNEL f1 ========
NUC1                  13C
P2                   8.60 usec
P15               1000.00 usec
PL1                  1.40 dB
PL11                 1.90 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.10 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229334 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Grain, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/11/2008   102.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME     KBSNRate_Grain103_6B
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_             20080611
Time                 23.01
INSTRUM              spect
PROBHD   4 mm MASxvt BB
PULPROG    cpnqs.99.LBA
TD                    1024
SOLVENT
NS                    3500
DS                       0
SWH              27777.777 Hz
FIDRES           27.126736 Hz
AQ               0.0185000 sec
RG                    3251
DW                  18.000 usec
DE                    6.00 usec
TE                   698.2 K
D1              2.00000000 sec
D3              0.00002500 sec

======== CHANNEL f1 ========
NUC1                   13C
P2                    8.60 usec
P15                1000.00 usec
PL1                   1.40 dB
PL11                  1.90 dB
SFO1            50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2             tppm15
NUC2                    1H
P3                    3.10 usec
P31                   5.10 usec
PL2                   6.00 dB
PL12                  3.00 dB
SFO2           200.1315000 MHz

F2 - Processing parameters
SI                   16384
SF              50.3229334 MHz
WDW                     EM
SSB                      0
LB                   30.00 Hz
GB                       0
PC                    1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Grain, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/14/2008   103.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.

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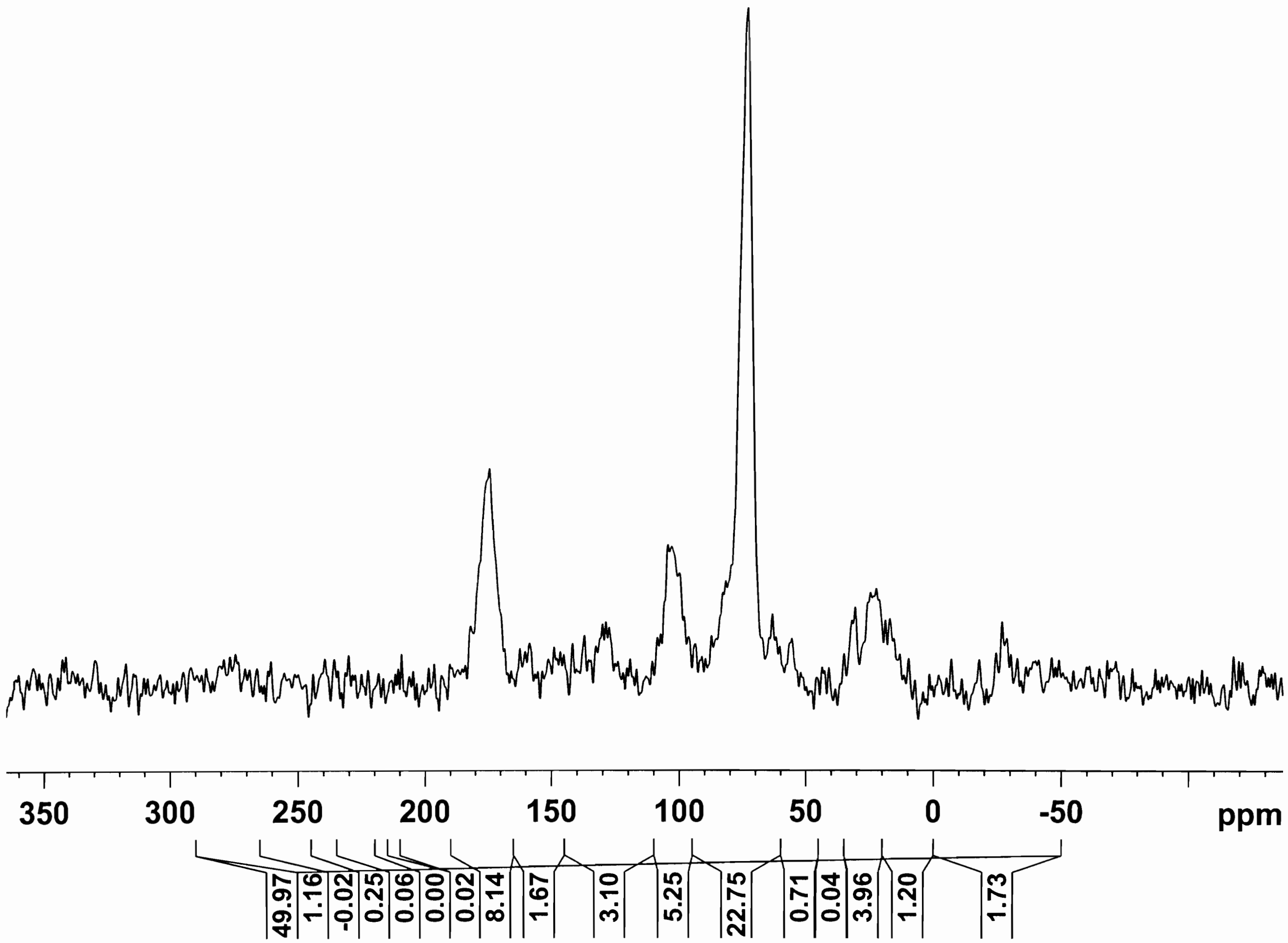


Current Data Parameters

NAME	KBSNRate_Grain105_7B
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20080314
Time	14.12
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cpnqs.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	1625.5
DW	19.800 usec
DE	6.00 usec
TE	694.5 K
D1	2.00000000 sec
D3	0.00002500 sec

======== CHANNEL f1 ========

NUC1	13C
P2	8.60 usec
P15	1000.00 usec
PL1	1.40 dB
PL11	1.90 dB
SFO1	50.3287071 MHz

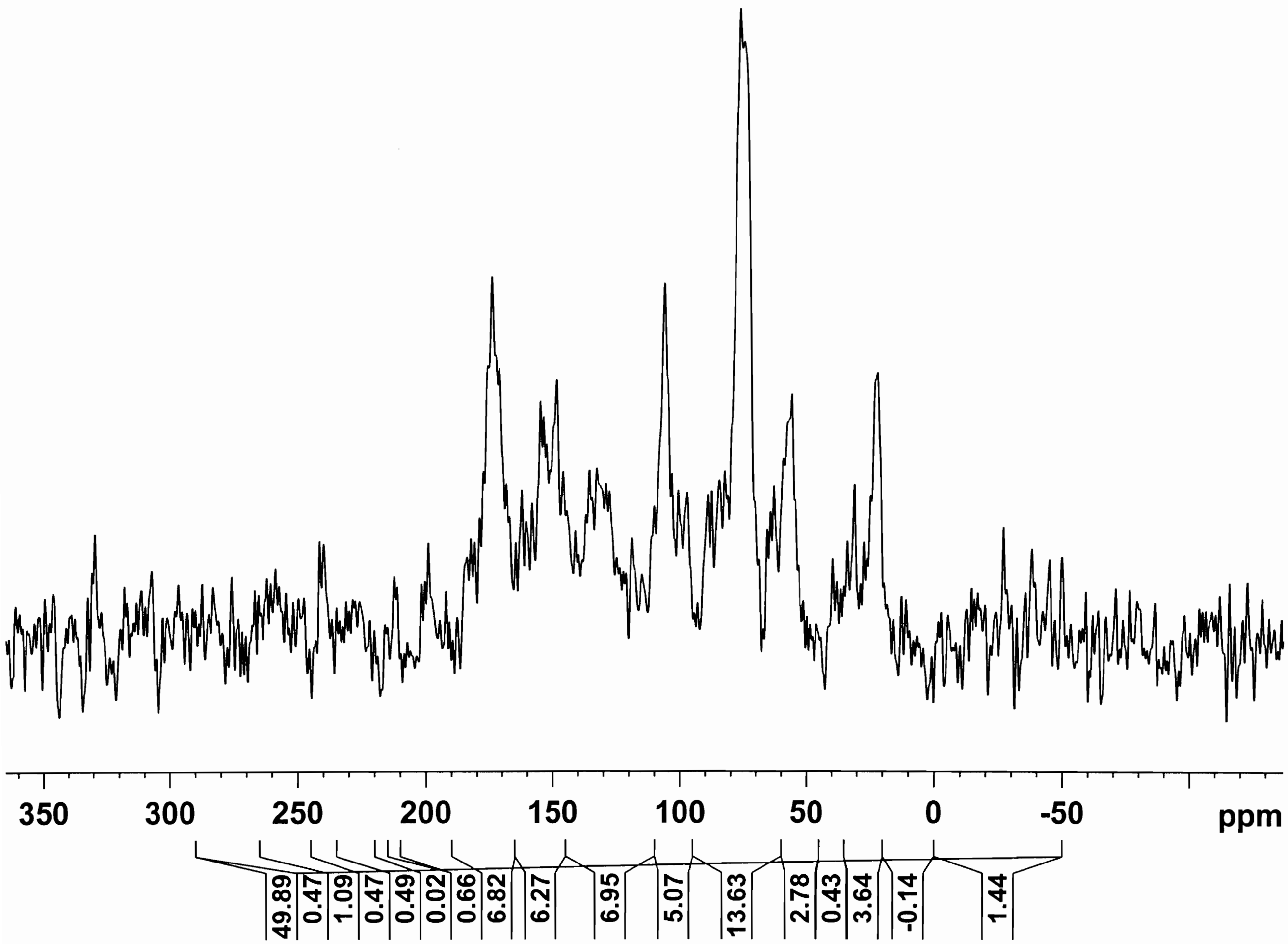
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229663 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1A Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, Cover Crop
03/10/2008 52.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_LS101_1A
EXPNO 2
PROCNO 1

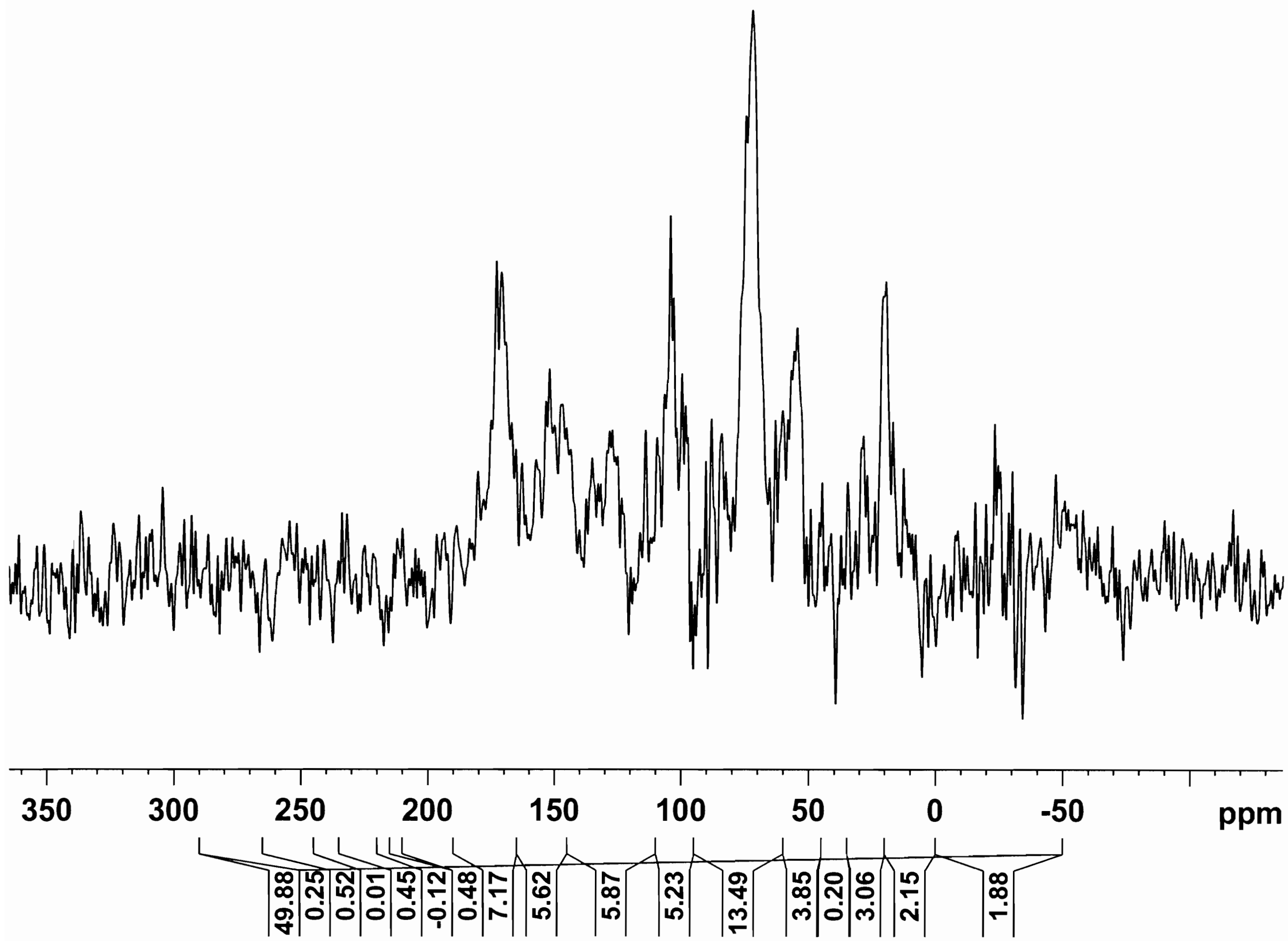
F2 - Acquisition Parameters
Date_ 20080310
Time 18.25
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 1149.4
DW 19.800 usec
DE 6.00 usec
TE 694.7 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

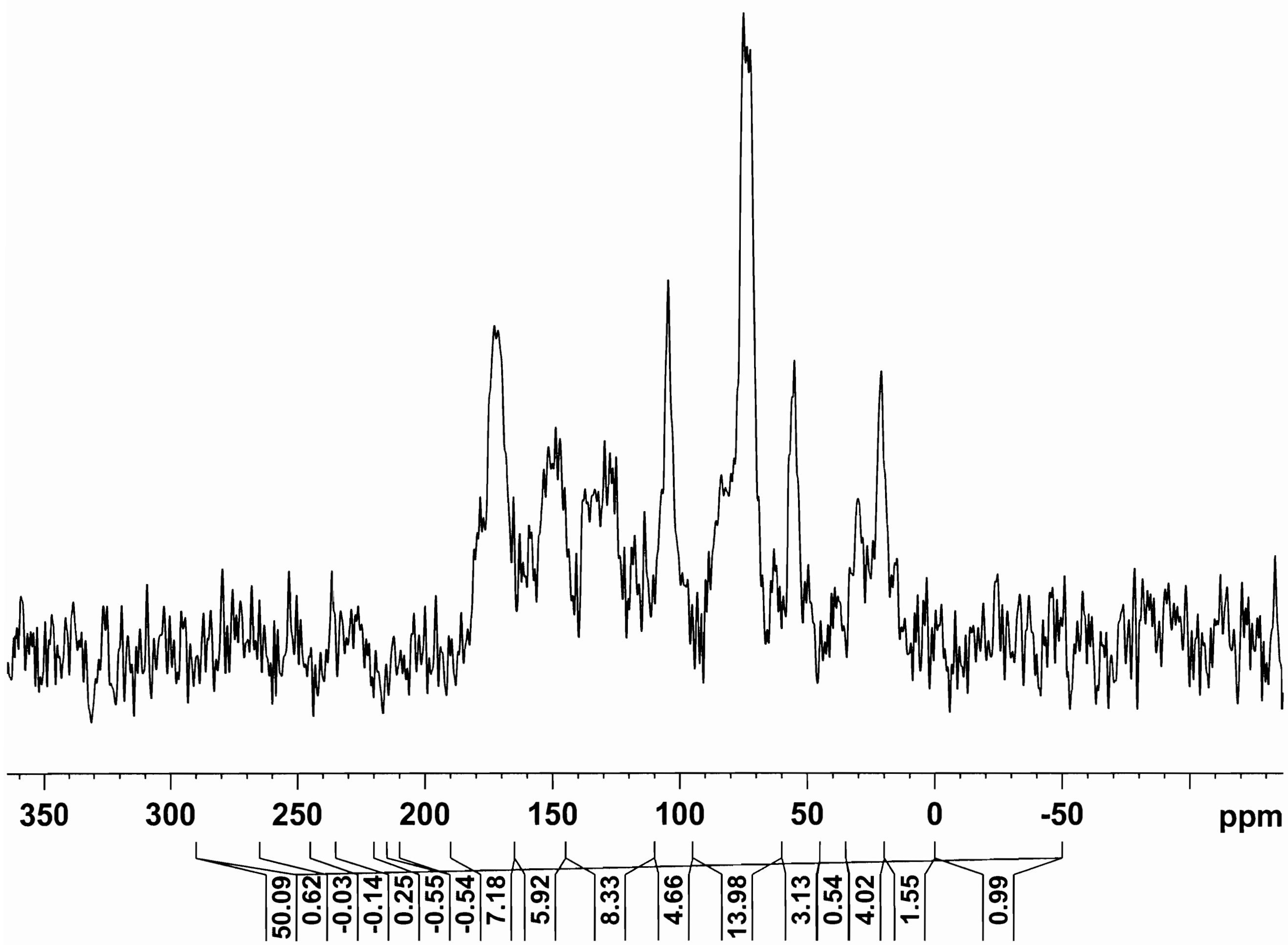
F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2A Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, Cover Crop
03/11/2008   53.0 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME       KBSNRate_LS107_2A
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20080311
Time                   18.54
INSTRUM                spect
PROBHD       4 mm MASxvt BB
PULPROG        cpnqs.99.LBA
TD                      1024
SOLVENT
NS                      3500
DS                         0
SWH                25252.525 Hz
FIDRES             24.660669 Hz
AQ                 0.0203450 sec
RG                    2298.8
DW                    19.800 usec
DE                      6.00 usec
TE                     697.2 K
D1                2.00000000 sec
D3                0.00002500 sec

======== CHANNEL f1 ========
NUC1                     13C
P2                      8.60 usec
P15                  1000.00 usec
PL1                     1.40 dB
PL11                    1.90 dB
SFO1              50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2               tppm15
NUC2                      1H
P3                      3.05 usec
P31                     5.10 usec
PL2                     6.00 dB
PL12                    3.00 dB
SFO2             200.1315000 MHz

F2 - Processing parameters
SI                     16384
SF                50.3229663 MHz
WDW                       EM
SSB                        0
LB                     30.00 Hz
GB                         0
PC                      1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3A Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, Cover Crop
03/07/2008   50.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



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Current Data Parameters
NAME KBSNRate_LS106_3A
EXPNO 2
PROCNO 1

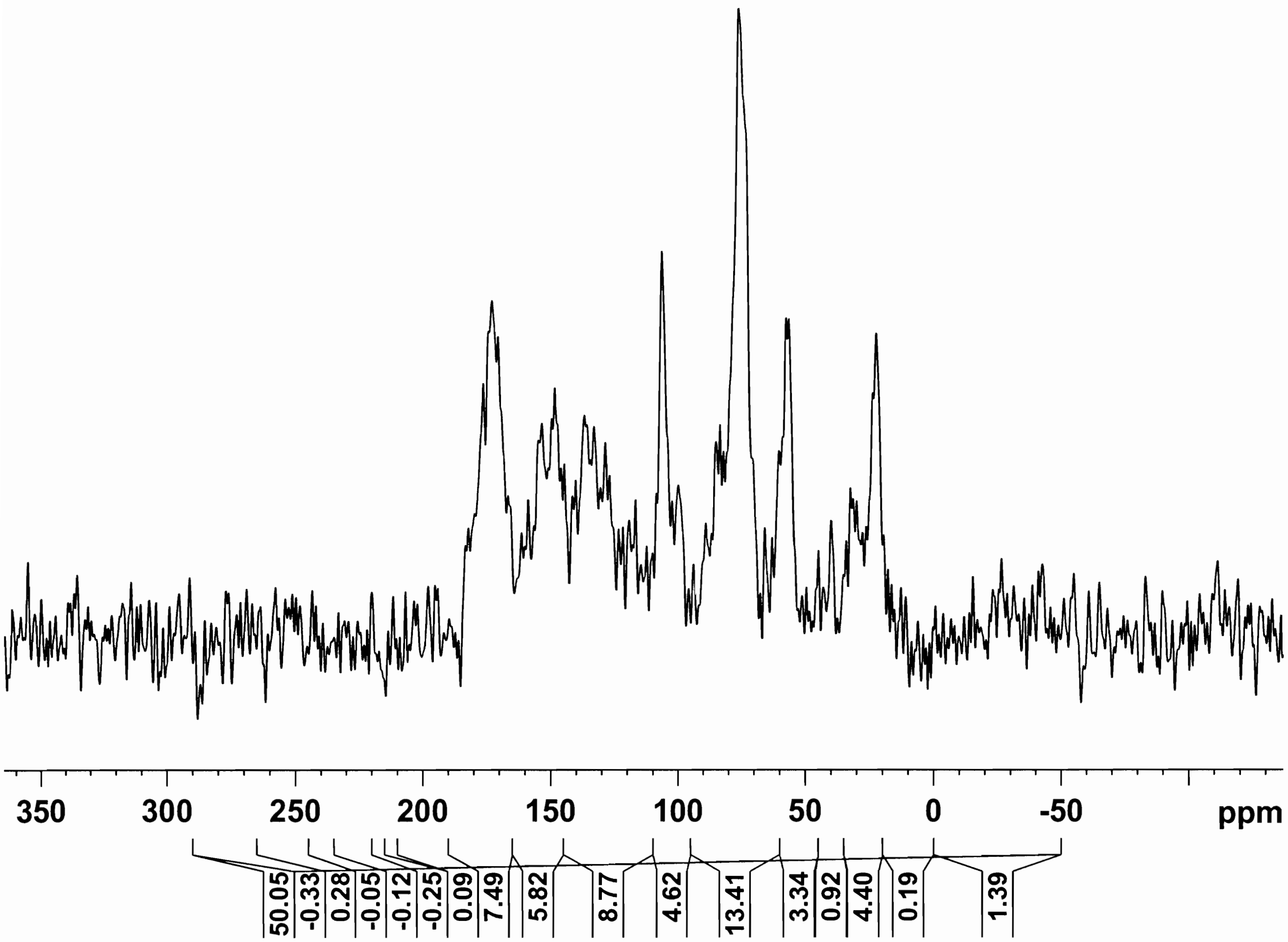
F2 - Acquisition Parameters
Date_ 20080307
Time 22.14
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 4597.6
DW 19.800 usec
DE 6.00 usec
TE 694.1 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4A Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, Cover Crop
03/08/2008 51.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_LS102_4A
EXPNO 2
PROCNO 1

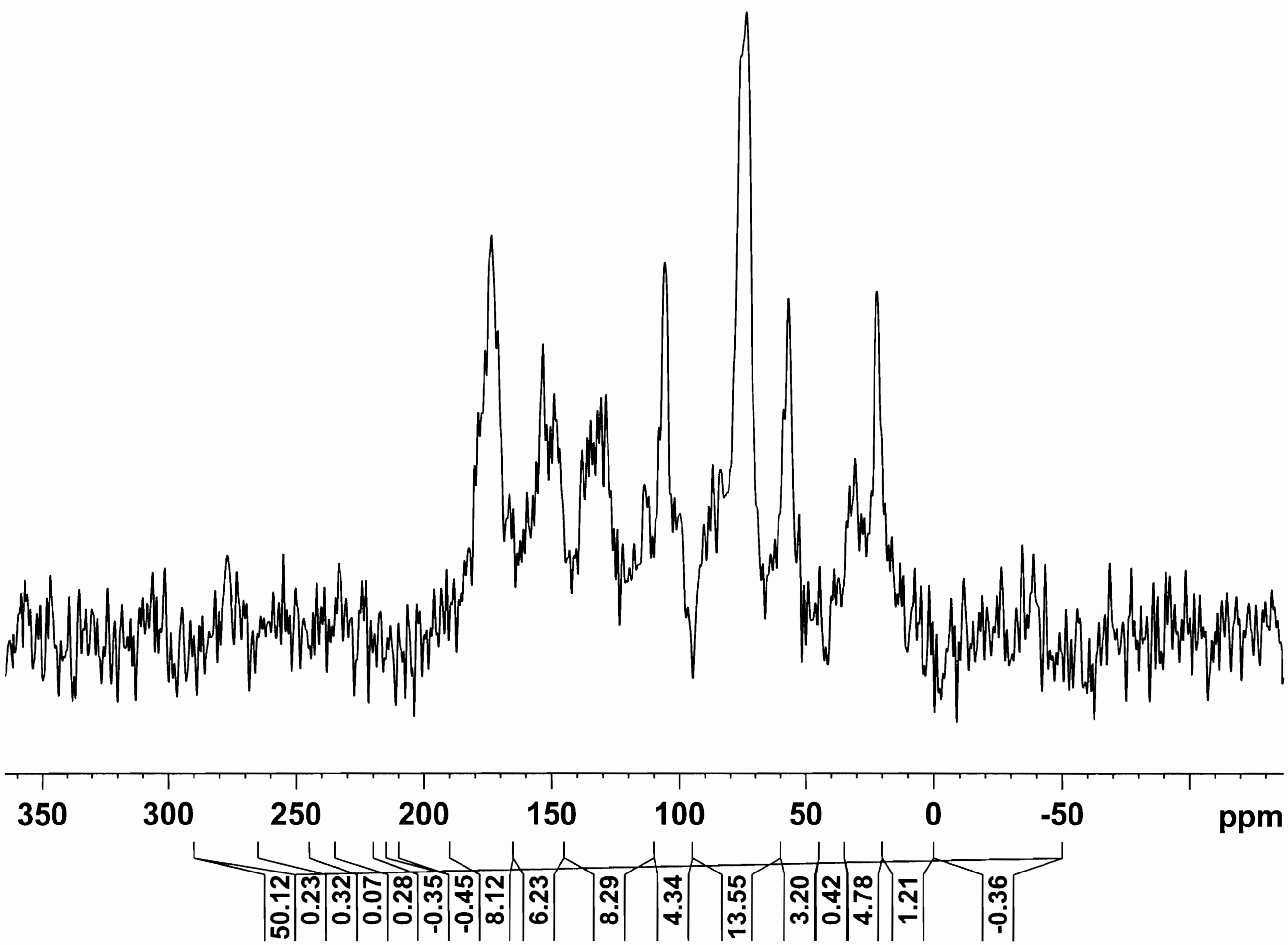
F2 - Acquisition Parameters
Date_ 20080308
Time 13.41
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2048
DW 19.800 usec
DE 6.00 usec
TE 694.2 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

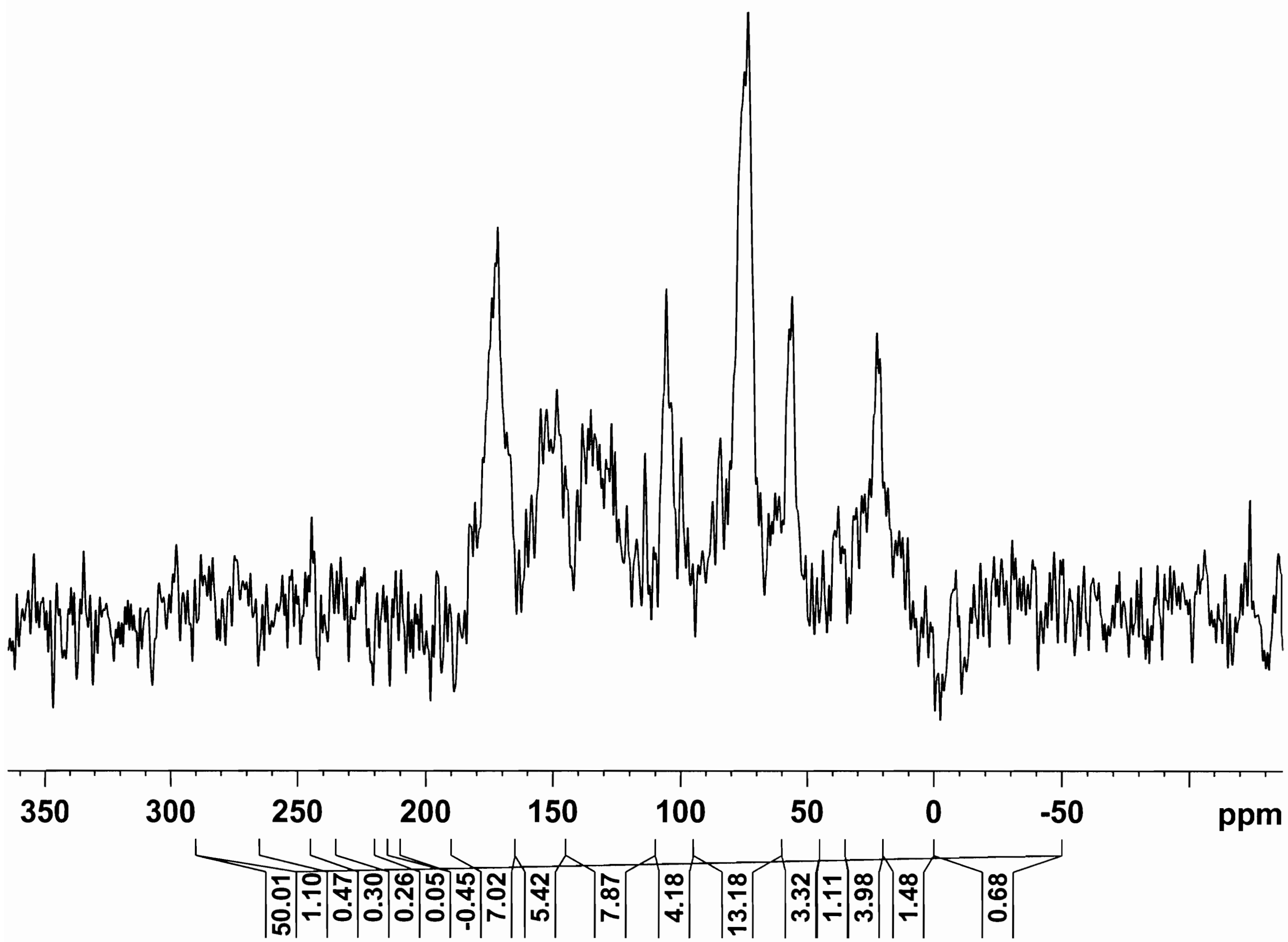
F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5A Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, Cover Crop
03/09/2008 49.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME      KBSNRate_LS104_5A
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_            20080309
Time                 6.00
INSTRUM             spect
PROBHD   4 mm MASxvt BB
PULPROG    cpnqs.99.LBA
TD                   1024
SOLVENT
NS                   3500
DS                      0
SWH             25252.525 Hz
FIDRES          24.660669 Hz
AQ              0.0203450 sec
RG                 1625.5
DW                 19.800 usec
DE                   6.00 usec
TE                  694.4 K
D1             2.00000000 sec
D3             0.00002500 sec

======== CHANNEL f1 ========
NUC1                  13C
P2                   8.60 usec
P15               1000.00 usec
PL1                  1.40 dB
PL11                 1.90 dB
SFO1           50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2            tppm15
NUC2                   1H
P3                   3.05 usec
P31                  5.10 usec
PL2                  6.00 dB
PL12                 3.00 dB
SFO2          200.1315000 MHz

F2 - Processing parameters
SI                  16384
SF             50.3229663 MHz
WDW                    EM
SSB                     0
LB                  30.00 Hz
GB                      0
PC                   1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6A Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, Cover Crop
03/09/2008   48.2 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



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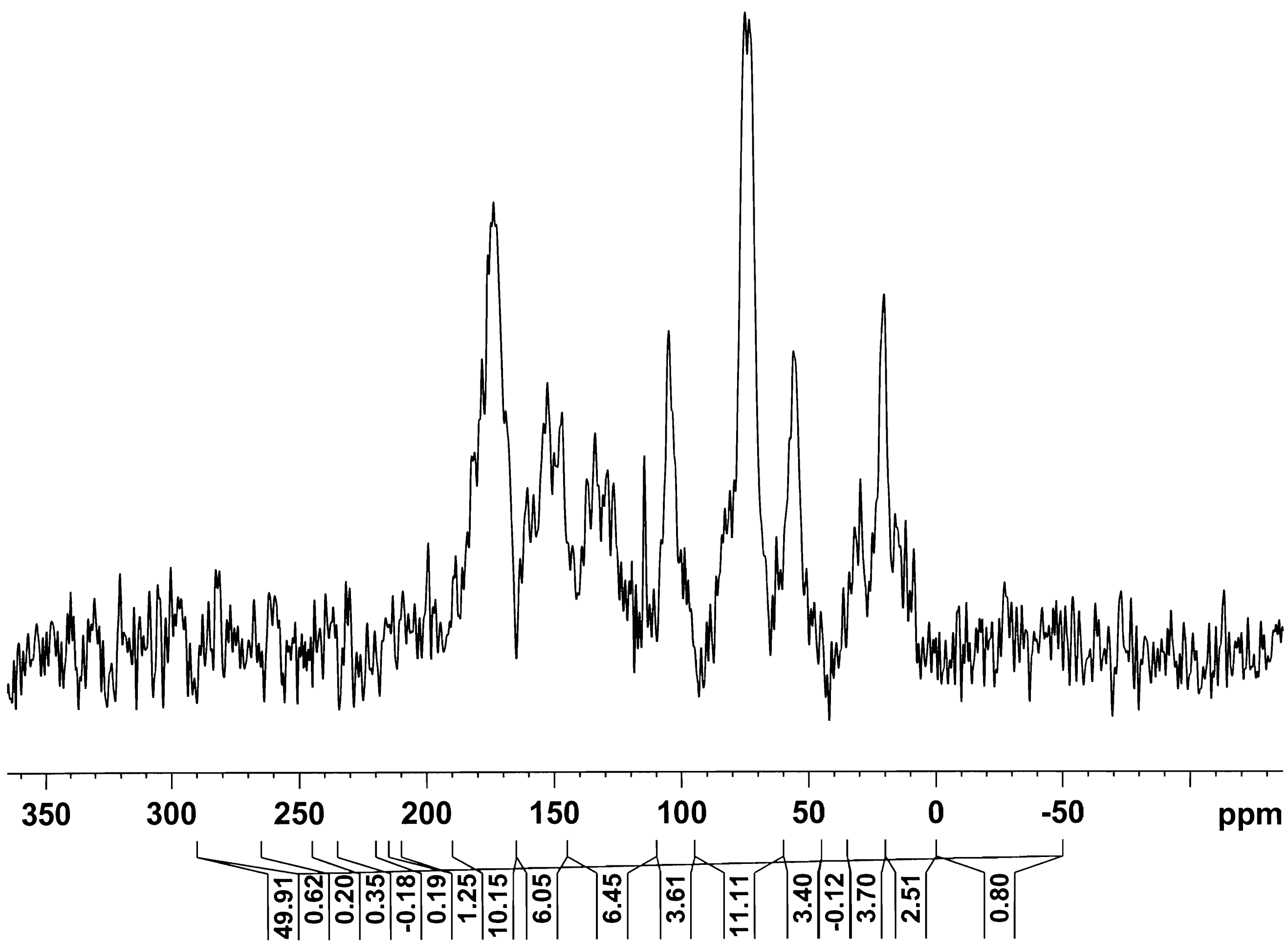
```
Current Data Parameters
NAME      KBSNRate_LS103_6A
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080309
Time                  21.10
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG      cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                   2580.3
DW                   19.800 usec
DE                     6.00 usec
TE                    694.6 K
D1               2.00000000 sec
D3               0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.05 usec
P31                    5.10 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229663 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

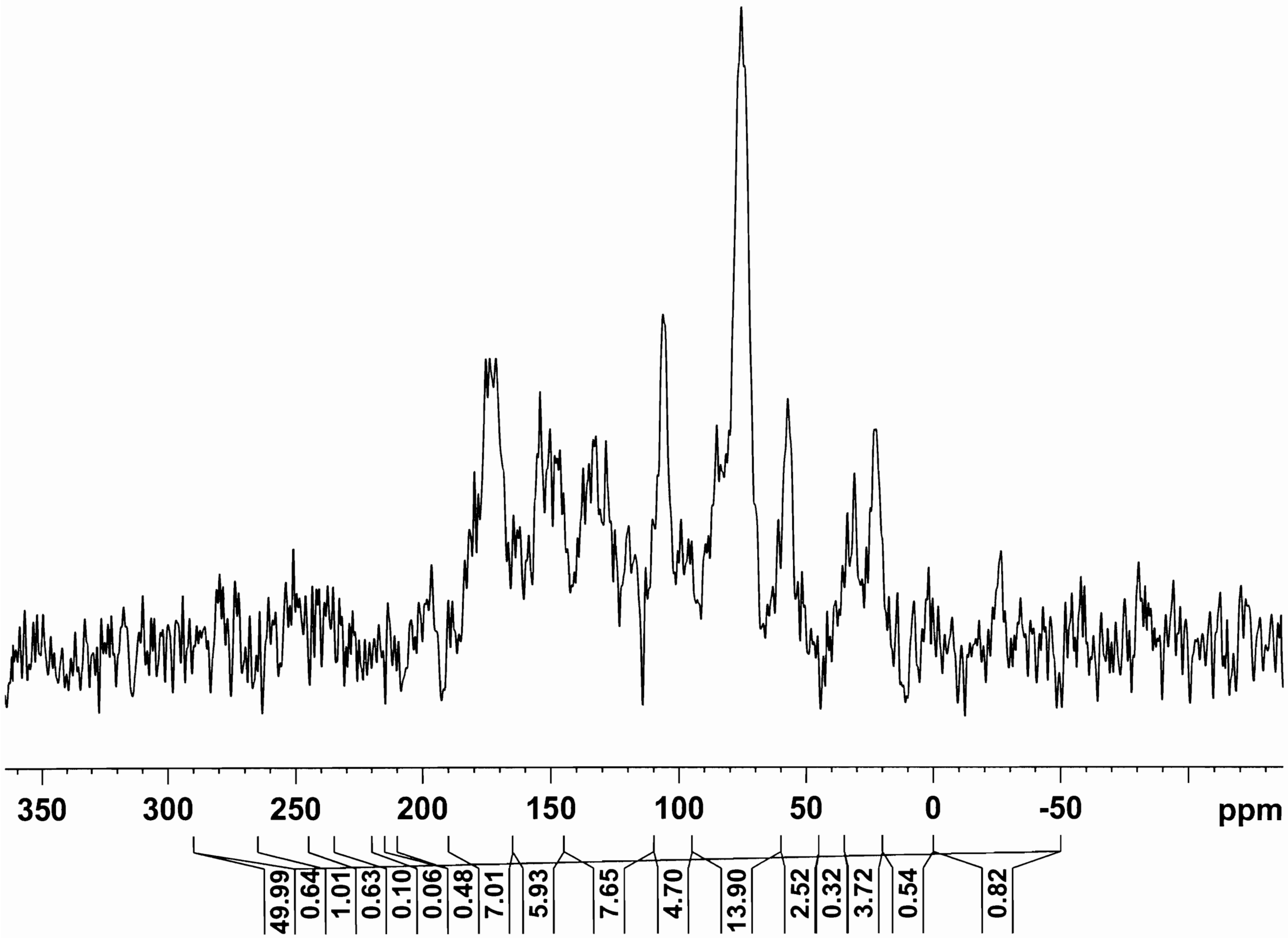
Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7A Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, Cover Crop
02/15/2008   52.3 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME      KBSNRate_LS105_7A
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080215
Time                  15.09
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG      cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                     2048
DW                   19.800 usec
DE                     6.00 usec
TE                    698.0 K
D1               2.00000000 sec
D3               0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.10 usec
P31                    5.00 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229351 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

455

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 101_1B Leaf&Stem, Treatment 0 kg N/ha, Replicate 1, No Cover Crop
03/15/2008   52.9 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters

NAME	KBSNRate_LS101_1B
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20080315
Time	6.03
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cpnqs.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	1149.4
DW	19.800 usec
DE	6.00 usec
TE	696.2 K
D1	2.00000000 sec
D3	0.00002500 sec

======== CHANNEL f1 ========

NUC1	13C
P2	8.60 usec
P15	1000.00 usec
PL1	1.40 dB
PL11	1.90 dB
SFO1	50.3287071 MHz

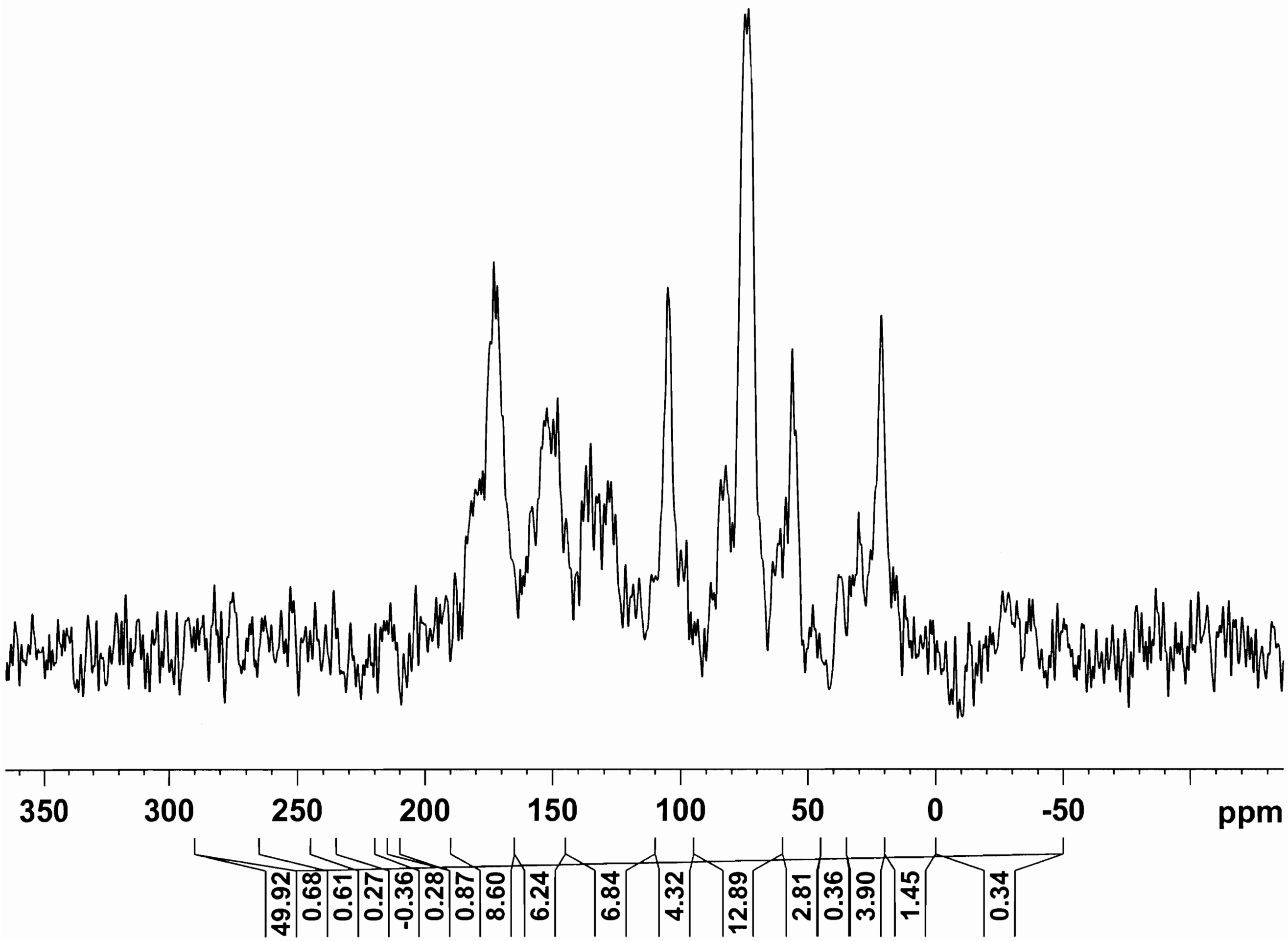
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.05 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

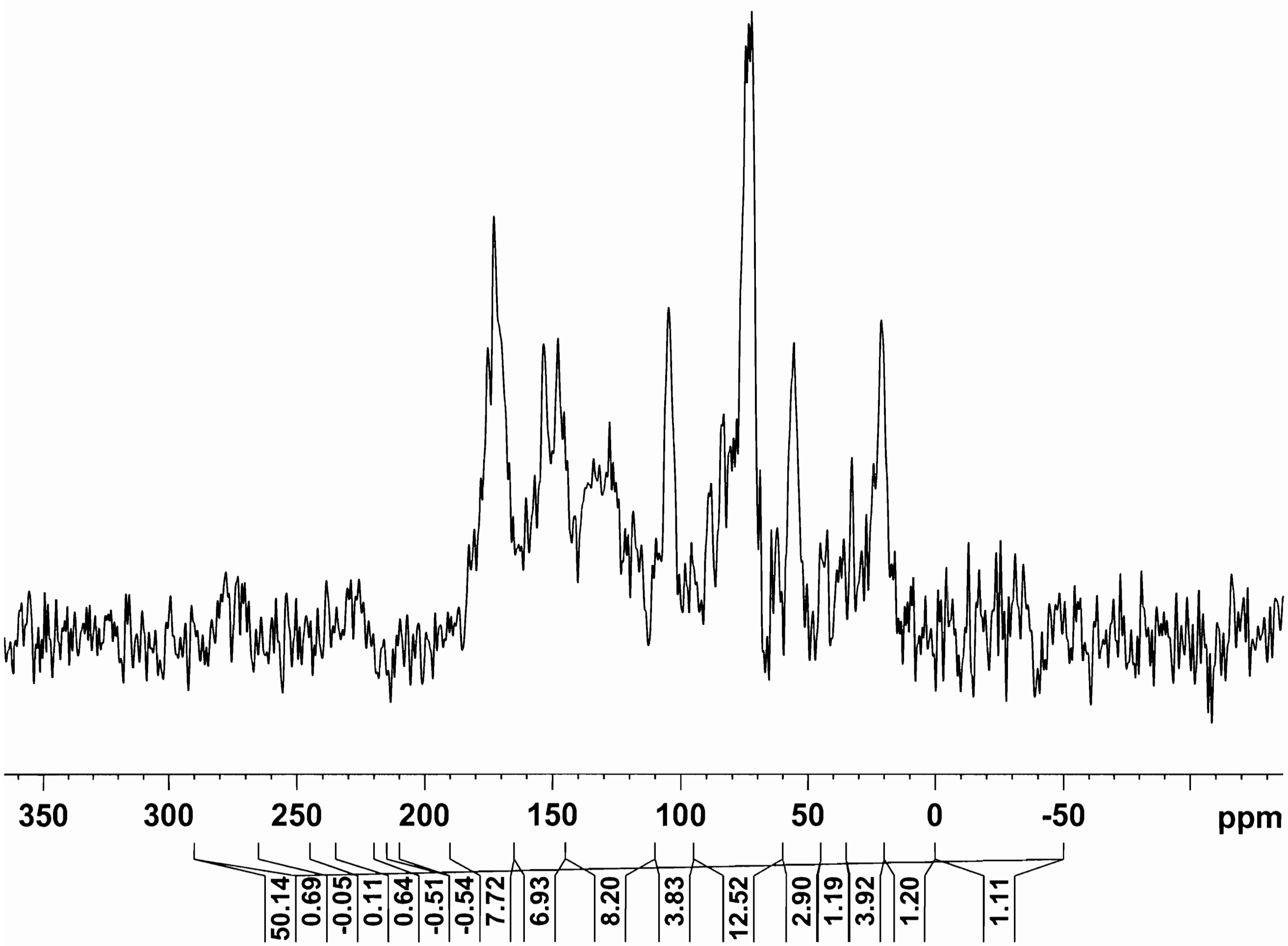
SI	16384
SF	50.3229663 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 107_2B Leaf&Stem, Treatment 34 kg N/ha, Replicate 1, No Cover Crop
06/28/2008   63.6 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



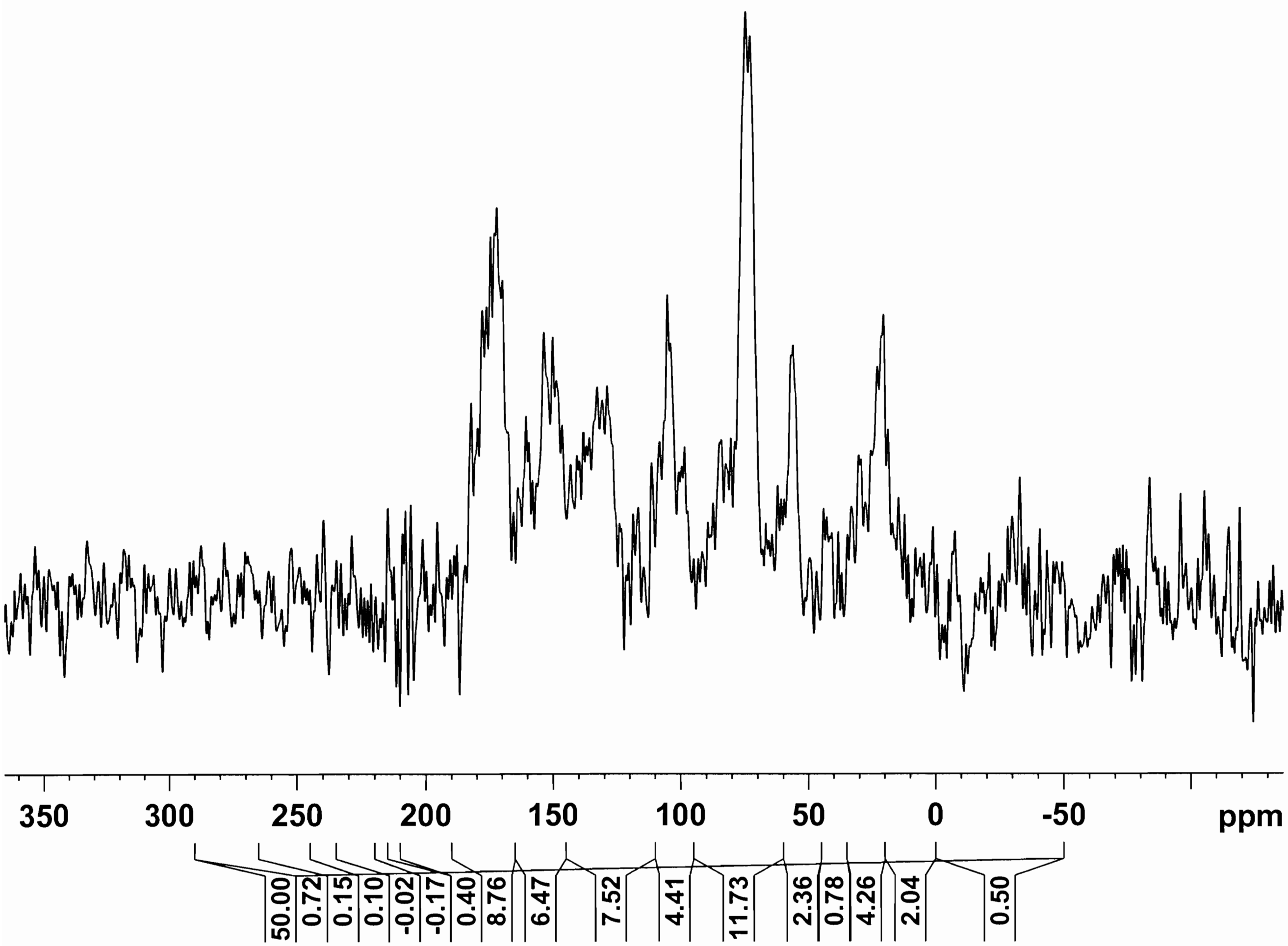

```
Current Data Parameters
NAME       KBSNRate_LS107_2B
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20080628
Time                  23.22
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG      cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                   1625.5
DW                   19.800 usec
DE                     6.00 usec
TE                    697.1 K
D1              2.00000000 sec
D3              0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.20 usec
P31                    5.10 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229331 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 106_3B Leaf&Stem, Treatment 67 kg N/ha, Replicate 1, No Cover Crop
06/24/2008   55.1 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



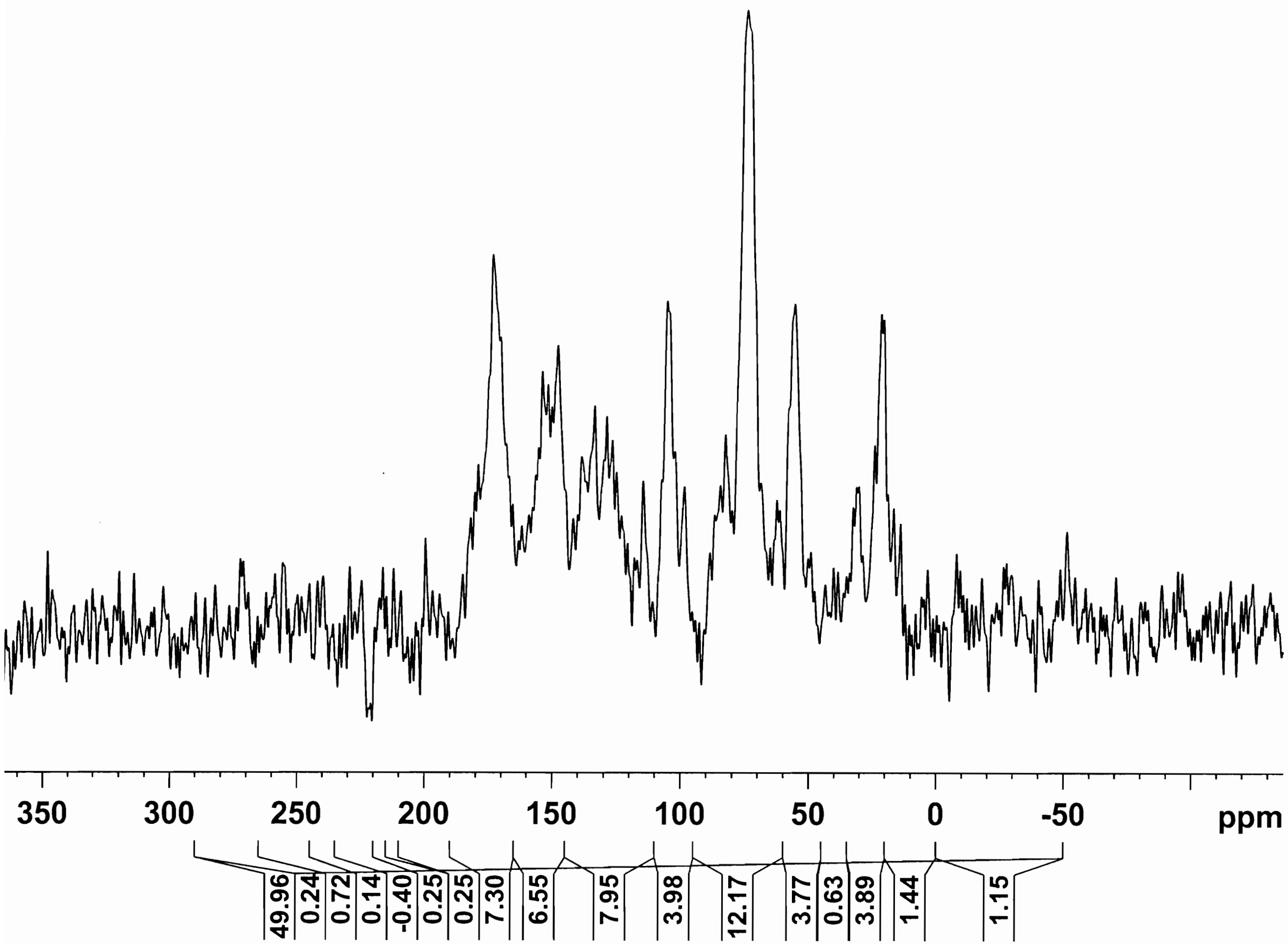

```
Current Data Parameters
NAME      KBSNRate_LS106_3B
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080625
Time                   0.58
INSTRUM               spect
PROBHD     4 mm MASxvt BB
PULPROG     cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                   1625.5
DW                   19.800 usec
DE                     6.00 usec
TE                    696.0 K
D1               2.00000000 sec
D3               0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.20 usec
P31                    5.10 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229331 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 102_4B Leaf&Stem, Treatment 101 kg N/ha, Replicate 1, No Cover Crop
06/25/2008   52.8 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



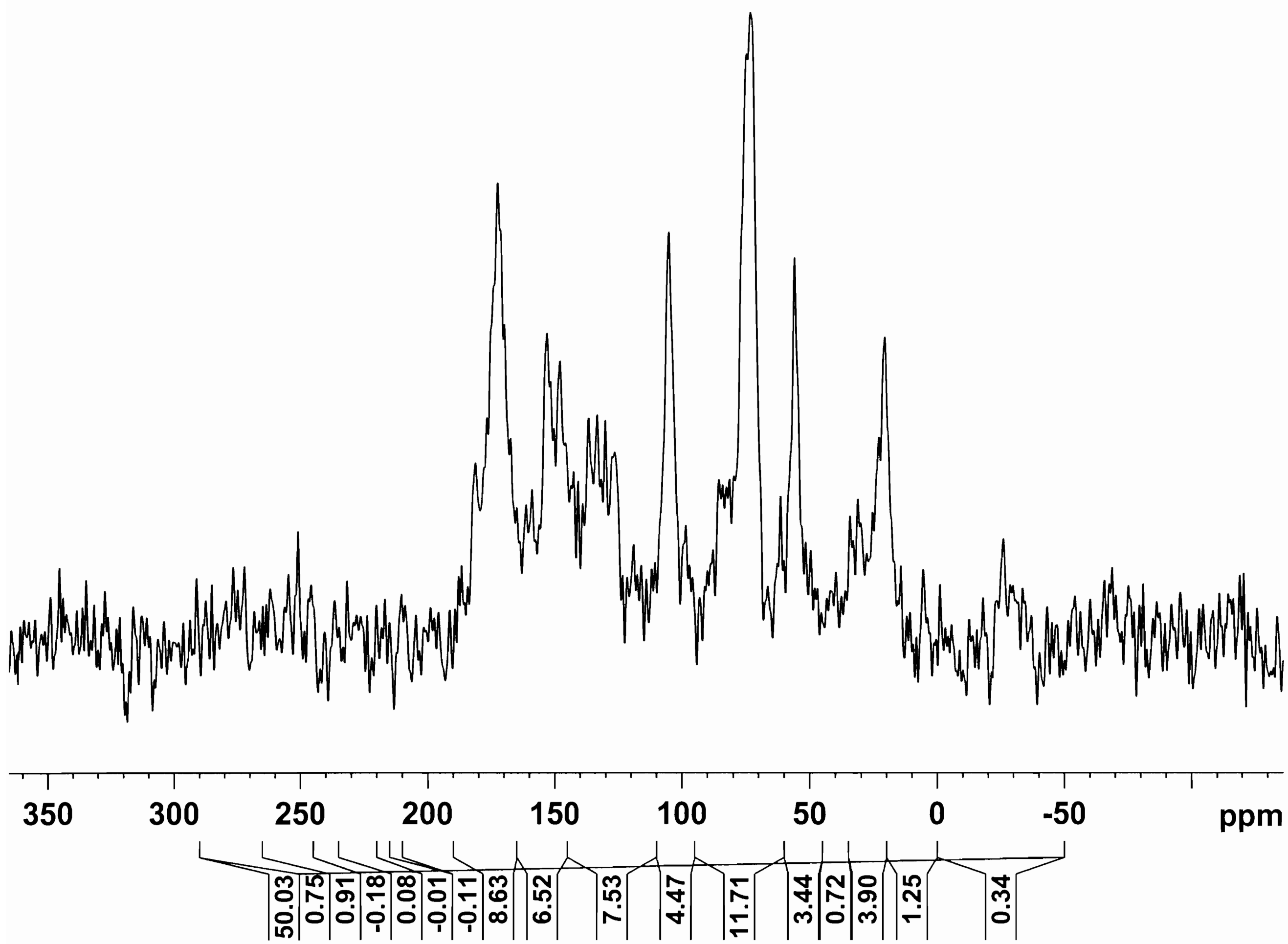

```
Current Data Parameters
NAME      KBSNRate_LS102_4B
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080625
Time                  21.02
INSTRUM               spect
PROBHD   4 mm MASxvt BB
PULPROG      cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH               25252.525 Hz
FIDRES            24.660669 Hz
AQ                0.0203450 sec
RG                   1625.5
DW                   19.800 usec
DE                     6.00 usec
TE                    695.9 K
D1               2.00000000 sec
D3               0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.20 usec
P31                    5.10 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229331 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 104_5B Leaf&Stem, Treatment 134 kg N/ha, Replicate 1, No Cover Crop
06/26/2008   51.4 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.




```
Current Data Parameters
NAME      KBSNRate_LS104_5B
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080626
Time                  21.10
INSTRUM               spect
PROBHD    4 mm MASxvt BB
PULPROG     cpnqs.99.LBA
TD                     1024
SOLVENT
NS                     3500
DS                        0
SWH              25252.525 Hz
FIDRES           24.660669 Hz
AQ               0.0203450 sec
RG                   1625.5
DW                   19.800 usec
DE                     6.00 usec
TE                    695.8 K
D1              2.00000000 sec
D3              0.00002500 sec

======== CHANNEL f1 ========
NUC1                    13C
P2                     8.60 usec
P15                 1000.00 usec
PL1                    1.40 dB
PL11                   1.90 dB
SFO1             50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2              tppm15
NUC2                     1H
P3                     3.20 usec
P31                    5.10 usec
PL2                    6.00 dB
PL12                   3.00 dB
SFO2            200.1315000 MHz

F2 - Processing parameters
SI                    16384
SF               50.3229331 MHz
WDW                      EM
SSB                       0
LB                    30.00 Hz
GB                        0
PC                     1.00
```

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 103_6B Leaf&Stem, Treatment 168 kg N/ha, Replicate 1, No Cover Crop
06/27/2008   56.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters

NAME	KBSNRate_LS103_6B
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20080627
Time	20.49
INSTRUM	spect
PROBHD	4 mm MASxvt BB
PULPROG	cpnqs.99.LBA
TD	1024
SOLVENT	
NS	3500
DS	0
SWH	25252.525 Hz
FIDRES	24.660669 Hz
AQ	0.0203450 sec
RG	1625.5
DW	19.800 usec
DE	6.00 usec
TE	697.0 K
D1	2.00000000 sec
D3	0.00002500 sec

======== CHANNEL f1 ========

NUC1	13C
P2	8.60 usec
P15	1000.00 usec
PL1	1.40 dB
PL11	1.90 dB
SFO1	50.3287071 MHz

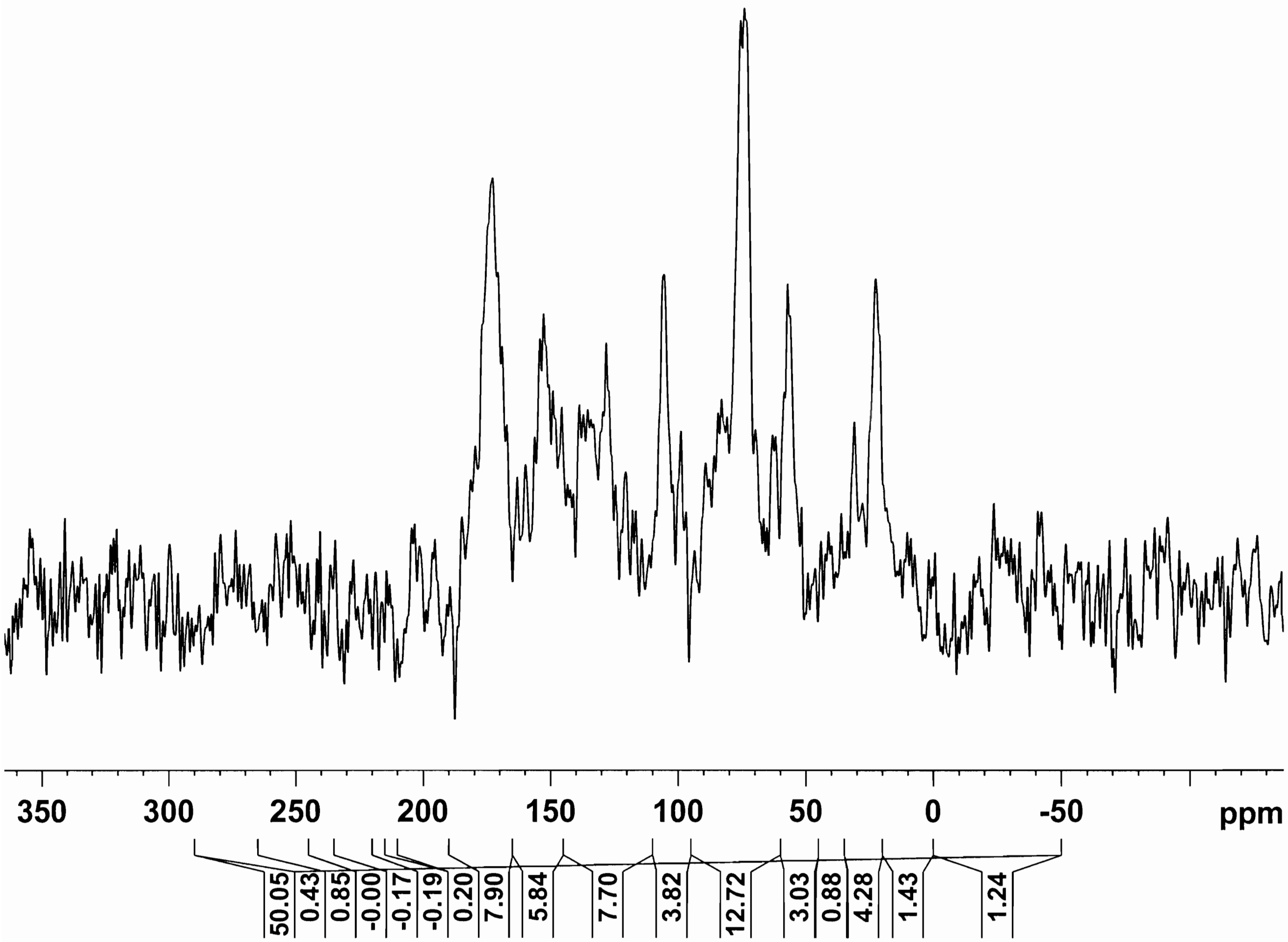
======== CHANNEL f2 ========

CPDPRG2	tppm15
NUC2	1H
P3	3.20 usec
P31	5.10 usec
PL2	6.00 dB
PL12	3.00 dB
SFO2	200.1315000 MHz

F2 - Processing parameters

SI	16384
SF	50.3229331 MHz
WDW	EM
SSB	0
LB	30.00 Hz
GB	0
PC	1.00

Corn Nitrogen Rate Experiment KBS-LTER Station
2006 105_7B Leaf&Stem, Treatment 202 kg N/ha, Replicate 1, No Cover Crop
03/15/2008 52.5 mg
4mm MAS probe. 5 kHz spin rate. CP/MAS+ 50us dipolar dephasing delay.



Current Data Parameters
NAME KBSNRate_LS105_7B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080315
Time 21.30
INSTRUM spect
PROBHD 4 mm MASxvt BB
PULPROG cpnqs.99.LBA
TD 1024
SOLVENT
NS 3500
DS 0
SWH 25252.525 Hz
FIDRES 24.660669 Hz
AQ 0.0203450 sec
RG 2580.3
DW 19.800 usec
DE 6.00 usec
TE 696.4 K
D1 2.00000000 sec
D3 0.00002500 sec

======== CHANNEL f1 ========
NUC1 13C
P2 8.60 usec
P15 1000.00 usec
PL1 1.40 dB
PL11 1.90 dB
SFO1 50.3287071 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.05 usec
P31 5.10 usec
PL2 6.00 dB
PL12 3.00 dB
SFO2 200.1315000 MHz

F2 - Processing parameters
SI 16384
SF 50.3229663 MHz
WDW EM
SSB 0
LB 30.00 Hz
GB 0
PC 1.00